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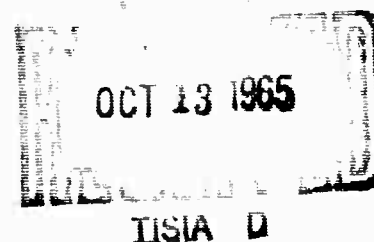
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CHEMILUMINESCENT MATERIALS

AMERICAN CYANAMID COMPANY
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STAMFORD, CONNECTICUT

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The following scientists made primary contributions to the technical effort:

M. M. Rauhut

L. J. Bollyky, R. A. Clarke, B. G. Roberts,
A. M. Semsel, R. H. Whitman, M. Loy.

Microanalyses were carried out under the direction of Dr. J. H. Deonarine; computer analyses under the direction of Dr. D. W. Behnken; infrared analyses by Mr. N. B. Colthup and by Mr. J. Falzone; other spectroscopic work was supervised by Dr. R. C. Hirt.

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SUMMARY

Progress toward the development of chemiluminescent systems is reported with particular reference to mechanistic studies of oxalyl chloride-hydrogen peroxide-fluorescer chemiluminescence and studies of several oxalyl peroxide chemiluminescent systems. Exploratory searches for new chemiluminescent systems are described.

A mechanistic study of the chemical processes involved in the oxalyl chloride-hydrogen peroxide-fluorescer chemiluminescent reaction has been completed and the mechanism of the reaction is discussed. A preliminary study is reported on the effects of reaction conditions on chemiluminescent intensities, lifetimes, quantum yields and radiation capacities of oxalic anhydride and oxalic ester reactions with hydrogen peroxide in the presence or 9,10-diphenylanthracene. Quantum yields were found to decrease with increasing concentration of the oxalic acid derivatives. A series of sixteen oxalic esters was examined qualitatively for chemiluminescence under a variety of reaction conditions. Superior results were found for esters containing electronegative substituents. Reactions of 5-hydroxytetrazole, octahydroxycyclobutane, and related compounds with hydrogen peroxide in the presence of 9,10-diphenylanthracene were not chemiluminescent.

INTRODUCTION

While the requirements for a practical chemical lighting system necessarily depend on a specific anticipated application, it is clear that for any given use a practical system must deliver light above a minimum specified intensity level for a specified length of time. The intensity and lifetime of a chemiluminescent system are related to the system's light capacity in lumen-hours liter⁻¹ by equation (1) where L is the light capacity, I is intensity in lumens, T is time in seconds and V is the volume of the system in liters.

$$(1) \quad L = \frac{\int_{T=0}^{T=\infty} I dt}{3600 V}$$

It is clear that L is a fundamental criterion for practical chemiluminescence, since a system where L is below some specified level cannot be made to meet the intensity-lifetime performance demanded by practicality.

While some chemiluminescent systems described in the literature meet certain requirements for practical lighting, all are deficient in terms of light capacity. The design of high light capacity systems is thus the primary goal of research directed toward practical chemical lighting.

Early efforts in this program coupled with a survey of the literature indicated a small probability at best of providing high light capacity systems through empirical modifications of chemical structure or reaction conditions of existing systems. It was also evident that available information on the mechanisms of chemiluminescent processes was inadequate for the deliberate

design of new systems. A program was therefore instituted to determine mechanistic and structural criteria for chemiluminescence so that high light capacity systems could be designed.

Our understanding of these criteria remains incomplete and work aimed at providing mechanistic information is continuing. However, mechanistic work now completed has already provided a substantial insight into the nature of chemiluminescence. The results of this work have been used to design chemiluminescent systems far superior in efficiency to those previously known. Thus, a major part of our current effort is being directed toward the discovery of efficient chemiluminescent systems, designed on the basis of newly derived mechanistic hypotheses, and the development of systems now in hand.

SECTION I

A STUDY OF CHEMILUMINESCENCE FROM REACTIONS OF OXALYL CHLORIDE, HYDROGEN PEROXIDE, AND FLUORESCENT COMPOUNDS

Although the direct conversion of chemical energy to light has been observed in a wide variety of chemical reactions,⁹ only a few reactions are known which provide moderately high chemiluminescent light intensities indicative of quantum yields above 10^{-3} . Prominent examples of such "bright" chemiluminescence include the reactions of hydrogen peroxide or oxygen with certain phthalhydrazide derivatives,^{10,11} imidazole derivatives^{12,13} and acridinium salts.^{6,7,8,14,15} Investigations of the mechanisms by which light is produced in such reactions has proved to be difficult because of the complex multistep processes involved and because of low quantum yields of emission. Thus, the identity of the key reaction step that produces the emitting singlet excited state in these reactions tends to be obscured by earlier reaction steps, subsequent reaction steps, and by competing non-luminescent side reactions. Even the identification of the emitting species in these reactions is subject to uncertainty since the available assignments rest entirely on comparisons of chemiluminescence and fluorescence spectral distributions in systems which lack well defined and uniquely characteristic emission bands. ^{2,3,5,8,11,13,15}

With these difficulties in mind, we have sought a model chemiluminescent reaction more suitable for mechanistic studies. The chemiluminescent reaction between oxalyl chloride, hydrogen peroxide and various fluorescent compounds, discovered by Chandross,¹⁶ appeared particularly attractive in this regard. Using aqueous hydrogen peroxide and a fluorescent aromatic hydrocarbon such as anthracene in an organic solvent, Chandross reported the emission as a bright flash having a color matching the fluorescence of the fluorescent additive. Thus, the emitting species, as Chandross suggested, appeared likely to be the singlet excited state of the fluorescer.

An adequate description of the overall mechanism of the oxalyl chloride-hydrogen peroxide-fluorescent compound system requires answering fundamental questions dealing with (1) the mechanisms of the chemical process involved, (2) the identity of the key reaction step where chemical energy is converted to electronic excitation energy and (3) the mechanism of the process by which the excitation energy appears as the singlet excited state of the emitter.

We have been investigating these questions for sometime. Although the third question remains unanswered and is still under study, this report completes our investigation of the chemical process involved in the chemiluminescent system. Thus, following the report of recent experiments below, we have summarized the pertinent results of the study and have provided an interpretation of these results in terms of a proposed reaction mechanism.

Recent Results

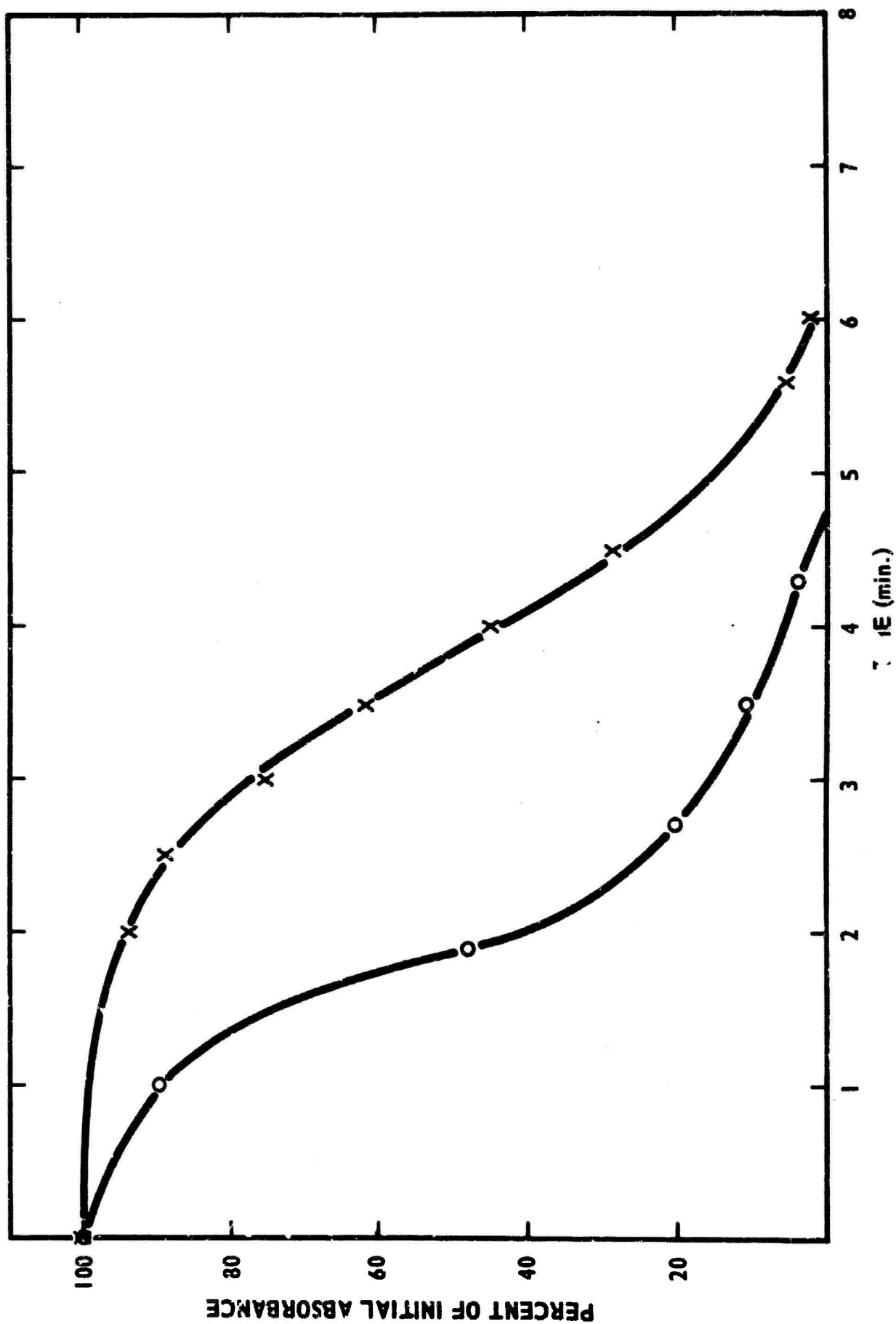
Infrared Spectroscopic Examination of Oxalyl Chloride-Hydrogen Peroxide Reactions

Several reactions in ether solution were analyzed spectrophotometrically for the rate of $\text{-}\overset{\text{O}}{\text{C}}\text{Cl}$ disappearance and for the rate of total carbonyl disappearance using absorption bands at 750 cm.^{-1} and 1790 cm.^{-1} respectively. Results obtained with oxalyl chloride and hydrogen peroxide concentrations of $0.75 \times 10^{-1}\text{ M}$ are pictured in Figure 1. It is seen that the rate of $\text{-}\overset{\text{O}}{\text{C}}\text{Cl}$ disappearance is substantially more rapid than the rate of total carbonyl disappearance. Thus while only 20% of the initial $\text{-}\overset{\text{O}}{\text{C}}\text{Cl}$ absorption remains after 2.7 mins., 89% of the initial carbonyl absorption remains.

Moreover, in a second experiment where the concentrations were $0.5 \times 10^{-1}\text{ M}$ oxalyl chloride and $1.0 \times 10^{-1}\text{ M}$ hydrogen peroxide, the $\text{-}\overset{\text{O}}{\text{C}}\text{Cl}$ formation could not be detected even at 30 seconds from the reaction start, while the rate of carbonyl disappearance was much the same as that pictured in Figure 1. It is clear from the results that oxalyl chloride disappears from the system far more rapidly than the overall reaction rate, particularly at high hydrogen peroxide-oxalyl chloride ratios, and that a carbonyl-containing product is formed, which reacts more slowly.

Figure 1

DISAPPEARANCE OF CHLOROCARBONYL AND TOTAL CARBONYL ABSORPTION BANDS
IN REACTION OF OXALYL CHLORIDE WITH HYDROGEN PEROXIDE IN ETHER (a)



NOTES TO FIGURE 1

a) Reaction of 0.75×10^{-1} M oxalyl chloride with 0.75×10^{-1} M hydrogen peroxide in ether.

○ = absorbance at 750 cm^{-1} ($\overset{\text{O}}{\text{CCl}}$)

x = absorbance at 1790 cm^{-1} ($\overset{\text{OO}}{\text{CC}}$)

Effect of Water on Quantum Yield and Reaction Rate in Dimethylphthalate Solution

Results showing the effect of water on reactions in dimethylphthalate solutions are summarized in Table I. As with experiments in ether⁸ it is seen that the initial intensity and the rate of intensity decay increased with increasing water concentration. Linear pseudo first order plots were not obtained until a substantial excess of water was present. It is clear, however, from the times required to reach one-half intensity, that the reaction is appreciably less rapid in dimethylphthalate than in ether. As indicated in Table I, added water reduced the time required for the intensity to reach the maximum value. In spite of the increase in maximum intensity with increasing water, the quantum yield decreased somewhat as a consequence of the shorter lifetime. When water addition was delayed 30 sec., the quantum yield of the aqueous portion of the reaction was essentially unchanged from the quantum yield when water was present initially. A 60 sec. delay in water addition, however, increased the quantum yield. It is clear from the results that quantum yields in dimethylphthalate are substantially higher than in ether.

The effect of water on the initial intensity indicates that water is a reactant in a step leading to chemiluminescent emission. The effect of water on the intensity decay rate indicates that water is involved in a rate determining step.

TABLE I

Effect of Water on Quantum Yield and Reaction Rate in Dimethylphthalate Solution^a

[H ₂ O] (Moles l. ⁻¹)	Time of Water Addition (sec)	Time to Reach Maximum Intensity (sec)	Time to Decay to 1/2 Intensity (sec)	Maximum Intensity (quanta sec. ⁻¹ ml. ⁻¹ x 10 ⁻¹⁴)	Quantum Yield (Einsteins mole ⁻¹)
0	-	15	56	8.6	4.69 x 10 ⁻²
0.51 x 10 ⁻²	0	12	45	10.1	4.64 x 10 ⁻²
2.54 x 10 ⁻²	0	10	26	12.9	3.91 x 10 ⁻²
3.55 x 10 ⁻²	0	8	26	14.5	3.97 x 10 ⁻²
3.55 x 10 ⁻²	30 sec.	--	--	--	4.10 x 10 ^{-2b}
3.55 x 10 ⁻²	60 sec.	--	--	--	4.47 x 10 ^{-2b}

a) Reactant concentrations were: oxalyl chloride, 2.42×10^{-3} M; H₂O₂, 0.15 M; DPA, 1×10^{-3} M; H₂O, 0.67×10^{-2} M. Temperature: 25°C.

b) Quantum yields were calculated by multiplying the measured quanta after 30 sec. or 60 sec. by the corresponding ratio obtained from the first experiment (total quanta/quanta after 30 sec.).

The Effect of Free Radical Inhibitors on Quantum Yield and Reaction Rate

Results of adding the free radical inhibitors 2,4-di-t-butyl-4-methylphenol (DTBMP)^{17,18} and styrene^{19,20,21} to oxalyl chloride-hydrogen peroxide-DPA reactions under a variety of conditions are summarized in Tables II and III. The results in Table II indicate that DTBMP seriously reduces quantum yields in both dimethylphthalate and ether solutions, but has little effect on reaction rates. The reduction in quantum yield is not a consequence of fluorescence quenching of DPA emission, since the fluorescence quantum yield of 4.6×10^{-4} M DPA in deoxygenated ether (0.82) was unchanged by the presence of 1.5×10^{-2} M DTBMP. The absence of an appreciable effect on the reaction rate indicates that, unlike ethanol, DTBMP does not reduce the quantum yield by competing with water in a rate determining step. Moreover, in contrast to water, delayed addition of DTBMP produced the same decrease in quantum yield as DTBMP present at the reaction start.

TABLE II

Effect of 2,6-di-t-butyl-4-methylphenol (DTBMP) on Quantum Yield and Reaction Rate in Dimethylphthalate (DMP) and Ether Solutions^a

$\frac{[\text{DTBMP}]}{(\text{mole l.}^{-1})}$	Solvent	Maximum Intensity ^b (quanta sec ⁻¹ ml ⁻¹ x 10 ⁻¹³)	First Half-life (sec)	Quantum Yield ^c (x 10 ³)	$\frac{\text{Q.Y. Inhibited}}{\text{Q.Y. Uninhibited}}$
0	DMP	48.6	87	41	-
0.67 x 10 ⁻³	DMP	36.6	95	38	0.98
2.00 x 10 ⁻³	DMP	25.2	84	23	0.59
10.0 x 10 ⁻³	DMP	7.2	85	6.5	0.17
15.0 x 10 ⁻³	DMP	6.1	73	4.8	0.12
15.0 x 10 ^{-3d}	DMP	----	----	4.7	0.12
0	Ether	1.3	24 ^e	0.35	----
30 x 10 ⁻³	Ether	0.59	25 ^e	0.12	.34
30 x 10 ^{-3d}	Ether	----	25 ^e	0.14	.40

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See following page for footnotes to table.

Footnotes to Table II

- a) Initial concentrations for DMP experiments: oxalyl chloride, 2.42×10^{-3} M; H_2O_2 , 0.20 M; DPA, 5.0×10^{-4} M. Initial concentrations for Ether experiments: oxalyl chloride, 2.18×10^{-3} ; H_2O_2 , 0.14 M; DPA, 2.3×10^{-4} . Temperature: 25°C.
- b) Measured at 430 mμ and corrected to total quanta.
- c) Based on oxalyl chloride.
- d) DTPMP added 30 seconds after reaction start; quantum yield calculated for inhibited portion of the reaction.
- e) Linear log intensity vs. time plots.

TABLE III

Effect of Hydrogen Peroxide Concentration on Quantum Yields and Reaction Rates of Inhibited Reactions in Ether^a

$[H_2O_2]$ (moles l^{-1})	A		B		C		Quantum Yield Ratios	
	Uninhibited Reaction k^1 (sec $^{-1}$) ($\times 10^2$)	Q.Y. ($\times 10^4$)	DTBMP Inhibitor ^b k^1 (sec $^{-1}$) ($\times 10^2$)	Q.Y. ($\times 10^4$)	Styrene Inhibitor ^c k^1 (sec $^{-1}$) ($\times 10^2$)	Q.Y. ($\times 10^4$)	B/A	C/A
1×10^{-2}	3.34	1.36	3.29	0.48	3.88	0.59	0.35	0.43
5×10^{-2}	3.57	.87	3.46	2.17	4.46	3.24	0.37	0.55
10×10^{-2}	3.84	10.5	3.72	4.1	4.38	5.14	0.39	0.49
20×10^{-2}	4.92	19.1	4.81	7.3	5.28	9.5	0.33	0.50

a) Initial concentrations: oxalyl chloride, 2.33×10^{-3} M; DPA, 5.0×10^{-4} M; water, 2.8×10^{-2} M at 25°C.

b) DTBMP concentration: 3×10^{-2} molar.

c) Styrene concentration: 4×10^{-1} molar.

Results showing the effects of DTBMP and styrene at varying hydrogen peroxide concentrations are summarized in Table III. It is seen that the ratio of inhibited to uninhibited quantum yields is not a function of hydrogen peroxide concentration, and that styrene is a less effective inhibitor than DTBMP.

DISCUSSION

The mechanism of the processes involving oxalyl chloride and hydrogen peroxide and the process leading to chemiluminescence must be consistent with the following observations.

(a) Disappearance of acyl chloride constituents from oxalyl chloride-hydrogen peroxide reaction mixtures in ether is fast relative to the disappearance of total carbonyl constituents and to the rate of intensity decay as indicated by infrared analysis.

(b) The quantum yield is essentially independent of the initial oxalyl chloride concentration at high hydrogen peroxide:oxalyl chloride ratios in ether.^{5,6,7,8} The expected quenching of fluorescent emission by oxalyl chloride is thus not observed, indicating early consumption of oxalyl chloride.

(c) The reaction rate is first order with respect to a derivative of oxalyl chloride as indicated by linear log intensity vs. time plots in ether where the ratio of oxalyl chloride to other reactants is low.⁵

(d) The overall reaction rate is independent of hydrogen peroxide concentration at least at low oxalyl chloride-hydrogen peroxide ratios.^{7,8}

(e) The quantum yield increases substantially with increasing hydrogen peroxide concentration even at high hydrogen peroxide concentrations when little water is present.^{5,6,7,8}

(f) The reaction rate increases substantially with increasing water concentration.^{7,8}

(g) The chemiluminescence intensity and quantum yield increases substantially with increasing water concentration in ether solution at low water levels even when water addition is delayed 30 seconds beyond the onset of reaction.^{7,8} The intensity increases with increasing water in dimethylphthalate although the quantum yield decreases.

(h) At moderate water concentrations in ether, the quantum yield is substantially higher when water is introduced after 30 seconds of reaction than when the same concentration of water is present initially.^{7,8} A 60 second delay is required for quantum yield increase in dimethylphthalate.

(i) The intensity decay rate is independent of fluorescer concentration.^{4,5}

(j) The quantum yield increases with increasing fluorescer concentration.^{3,5,7}

(k) The singlet excited state of the fluorescer is the emitting species.^{3,6,7}

(l) Chemiluminescence does not require consumption of the fluorescer.^{3,6}

(m) The chemiluminescence quantum yield is reduced by 2,6-di-t-butyl-4-methylphenol (DTBMP) and by styrene but the yield loss does not stem from reactions of DTBMP with acid chloride or from fluorescence quenching of DPA emission by DTBMP.

(n) The overall reaction rate is not substantially altered by 2,6-di-t-butyl-4-methylphenol.^{7,8}

(o) Quantum yields are substantially higher in dimethylphthalate solution than in ether, although reaction rates are substantially slower.⁵

(p) The major reaction products are hydrochloric acid, carbon monoxide, and carbon dioxide.^{3,4} Oxygen was not found in significant amounts.

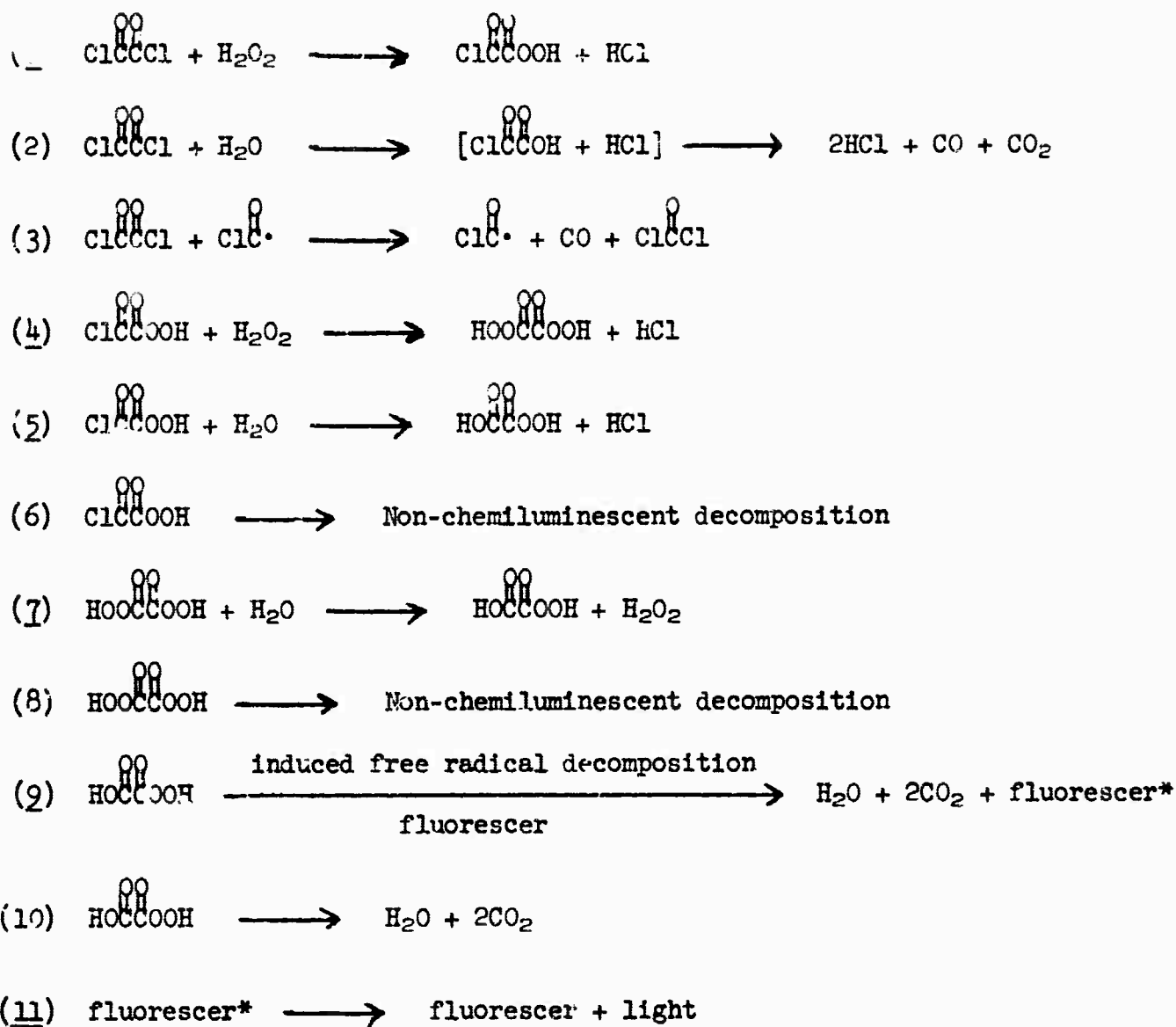
(q) Phosgene is a product in dimethylphthalate solution at high oxalyl chloride concentrations when the ratio of hydrogen peroxide to oxalyl chloride is low.⁴

A partial mechanism for the overall process in accord with the above observations is suggested in Chart A. The proposed steps leading to chemiluminescence are underlined to distinguish them from non-luminescent side reactions. The mechanism is not a complete description of the process since the evidence at hand does not permit a detailed analysis of steps (6), (8), (9), and (10), although all of these steps have close analogies.

The mechanistic steps in Chart A are seen to include the bulk of all possible reactions between oxalyl chloride, hydrogen peroxide, and water. The following argument is designed to show that all of these steps are indicated by the experimental data and to show that the results permit a selection of those steps leading to chemiluminescence.

CHAPT A

Proposed Partial Mechanism



Steps (1) through (6) involve reactions of acyl chlorides and in ether solution are evidently complete prior to the bulk of light emission as indicated by the separate observations (a), (b), (c), (d), and (h). Thus, (a) indicates by direct observation that acid chloride disappears from the chemiluminescent system more rapidly than a carbonyl-containing intermediate and more rapidly than light decay; (b) and (c) indicate the absence of fluorescence quenching of DPA by oxalyl chloride in the chemiluminescent experiments although fluorescence quenching would occur if oxalyl chloride were present; (d) indicates that reactions of hydrogen peroxide are not rate determining, and since reactions involving hydrogen peroxide would be expected in the early steps, such reactions must be essentially complete prior to light emission; and (h) indicates that direct reaction of hydrogen peroxide with oxalyl chloride is substantially reduced when water addition is delayed.

The less extensive results from experiments in dimethylphthalate, where solvent absorption prevented spectroscopic determination of acid chloride disappearance, suggest that oxalyl chloride consumption is less rapid than in ether. Thus, linear first order plots were not obtained until substantial excesses of water and hydrogen peroxide were present, and the effect of delayed water addition on quantum yield was minor relative to the effect in ether.

Step (2) [and the analogous step (5)] seem required by the increase in quantum yield provided by delayed water addition (h). The reaction of oxalyl chloride with water has been reported to give carbon monoxide and carbon dioxide rapidly and quantitatively and attempts to trap the intermediate mono acid chloride with aniline have been reported to be unsuccessful.²² Since hydrogen peroxide is substantially more reactive than water in nucleophilic reactions,²³ steps (1) and (4) should dominate steps (2) and (5) at high hydrogen peroxide:water ratios.

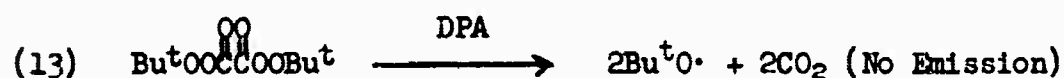
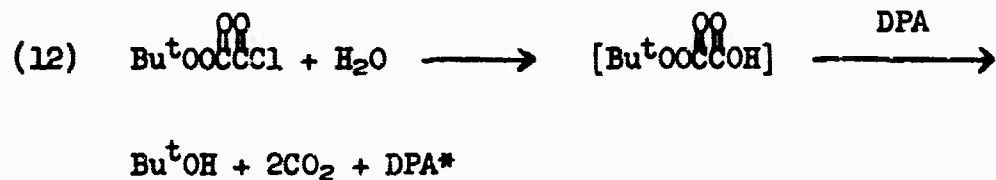
Step (3) is included to accommodate phosgene formation in dimethylphthalate solution (q), and induced decomposition of oxalyl chloride may also occur in ether. However, at high hydrogen peroxide:oxalyl chloride ratios such reactions should be of minor importance.

Competitive steps (4) and (6) seem required by the pronounced increase in quantum yield with increasing hydrogen peroxide concentration (e). This result is not accounted for by competitions between hydrogen peroxide and water in steps (1) and (2) or in steps (4) and (5) since the effect of hydrogen peroxide concentration on quantum yield remains large even at high hydrogen peroxide:water ratios where steps (1) and (4) are already dominant.²³ Observation (e) thus suggests a separate non-luminescent reaction involving chloroperoxyoxalic acid but not involving hydrogen peroxide or water. A rapid spontaneous decomposition of chloroperoxyoxalic acid, as indicated in step (6), seems reasonable in view of the rapid decomposition.

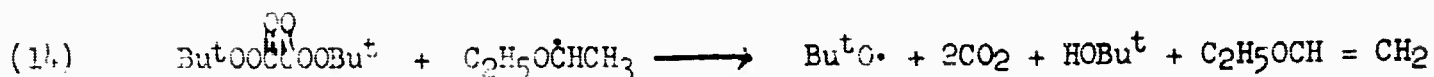
of chlorooxalic acid²² (step 2) and the general instability of peroxyoxalate derivatives^{20,24,25}. Thus, according to Chart A, increasing hydrogen peroxide favors step (4) over step (6) and increases the quantum yield. Step (6) probably involves a decomposition to the $\text{Cl}\overset{\text{O}}{\underset{\cdot}{\text{C}}}\cdot$ and $\cdot\text{OH}$ radicals along with CO_2 . The $\text{Cl}\overset{\text{O}}{\underset{\cdot}{\text{C}}}\cdot$ radical [through hydrogen abstraction and in step (3)] is a likely source of the carbon monoxide observed at low hydrogen peroxide: oxalyl chloride ratios [observation (p)]. Our failure to observe oxygen as a significant product would appear to rule out decomposition of chloro-peroxyoxalic acid by a cyclic transition state involving direct HCl formation¹⁶.

Step (7) seems required by observations (g) and (h) and by observations (a), (c), and (f). The increase in intensity with increasing water concentration (g) demonstrates that water is involved in a step leading to chemiluminescence. This step cannot be step (5) alone, since the increase in intensity is even more pronounced when water addition is delayed (h) beyond the time when acid chlorides are detected (a). Moreover, observations (a) and (c) indicate that the rate determining step involves a non-acid chloride carbonyl intermediate and observation (f) indicates that it involves water. The rate-determining step involving water can not be a step where hydrogen peroxide is in competition, since hydrogen peroxide is not involved in a rate-determining step (d).

Step (8) seems required, at least in ether solution, by observation (g) since added water acting in step (7) would increase the reaction rate and the light intensity but not the quantum yield in the absence of a competing non-luminescent decomposition of diperoxyoxalic acid. The spontaneous decompositions in steps (6) and (8) seem reasonable in view of the poor stability of peroxyoxalates^{20,24,25}. The assignments of a chemiluminescent role to step (7) and a non-chemiluminescent role to step (8) are suggested further by the observations that the reaction of t-butylperoxyoxalyl chloride with hydrogen peroxide in the presence of DPA is strongly chemiluminescent while the decomposition of di-t-butyldiperoxyoxalate under identical conditions is not chemiluminescent.³



Since a rapid decomposition of acyl peroxide is known to be specifically induced by ether (equation 14)^{17,19,20,26}, ether induced decomposition in steps (6) and (8) might account for the low quantum yields in ether relative to dimethylphthalate (o).



However, ether-induced decompositions of simple acyl peroxides¹⁹, and of di-t-butyldiperoxyoxalate²⁰ are eliminated by the addition of styrene, and styrene has relatively little effect on the reaction reported here. It is possible, however, that diperoxyoxalic acid is a better radical trap than styrene or DTBMP, and that its induced decomposition is not readily subject to inhibition. Indeed, step (9) appears to involve induced decomposition, as discussed below, and yet is not entirely inhibited by large amounts of inhibitor. As noted in Table II, inhibitors reduce the quantum yield less in ether solution than in dimethylphthalate, suggesting that in ether inhibition of step (9) is partly compensated by inhibition of induced decomposition in step (8).

Competing steps (9) and (10) seem required to account for the increase in quantum yield with increasing fluorescer concentration (j). Step (9) appears to involve an induced free radical decomposition in both ether and in dimethylphthalate in view of the observed effects of free radical inhibitors (m). Since steps (6) and (8) might also be subject to induced decomposition^{20,27} and its inhibition, the effect of inhibitors in reducing the quantum yield may indicate that induced decomposition in step (9) is more readily inhibited than in steps (6) or (8). In any event it is clear that, while the effect of inhibitor increases with inhibitor concentration, inhibition is incomplete even at relatively high inhibitor concentrations. Moreover, even when inhibited, step (9) is not rate-determining (n).

The detailed mechanism represented by step (9) is currently under investigation. The evidence presently available permits at least two alternative possibilities. (1) The decomposition of a complex of the fluorescer with monoperoxyoxalic acid, so that the formation of excited fluorescer would be synchronous with decomposition; (2) The decomposition of monoperoxyoxalic acid to excited carbon dioxide followed by transfer of singlet excitation energy to the fluorescer. The latter is a particularly attractive possibility, since excited carbon dioxide has been shown to be responsible for chemiluminescent emission in certain vapor phase reactions²⁸, and singlet excitation energy is known to undergo efficient transfer in a number of systems^{29,30}.

Step (9), according to either of the possibilities, does not require consumption of the fluorescer in accordance with observation (1), and step (11) accommodates the observed emission from the excited singlet state of the fluorescer (observation k).

Under conditions where hydrogen peroxide is in substantial excess to water and where the oxalyl chloride concentration is small, the rate of steps (1), (2), (3), and (5) will have little influence on the quantum yield. These conditions are approximately met in Tables II and III and in previous results^{7,8}. Under such conditions the mechanism in Chart A predicts a quantum yield relationship of the form of equation (a).

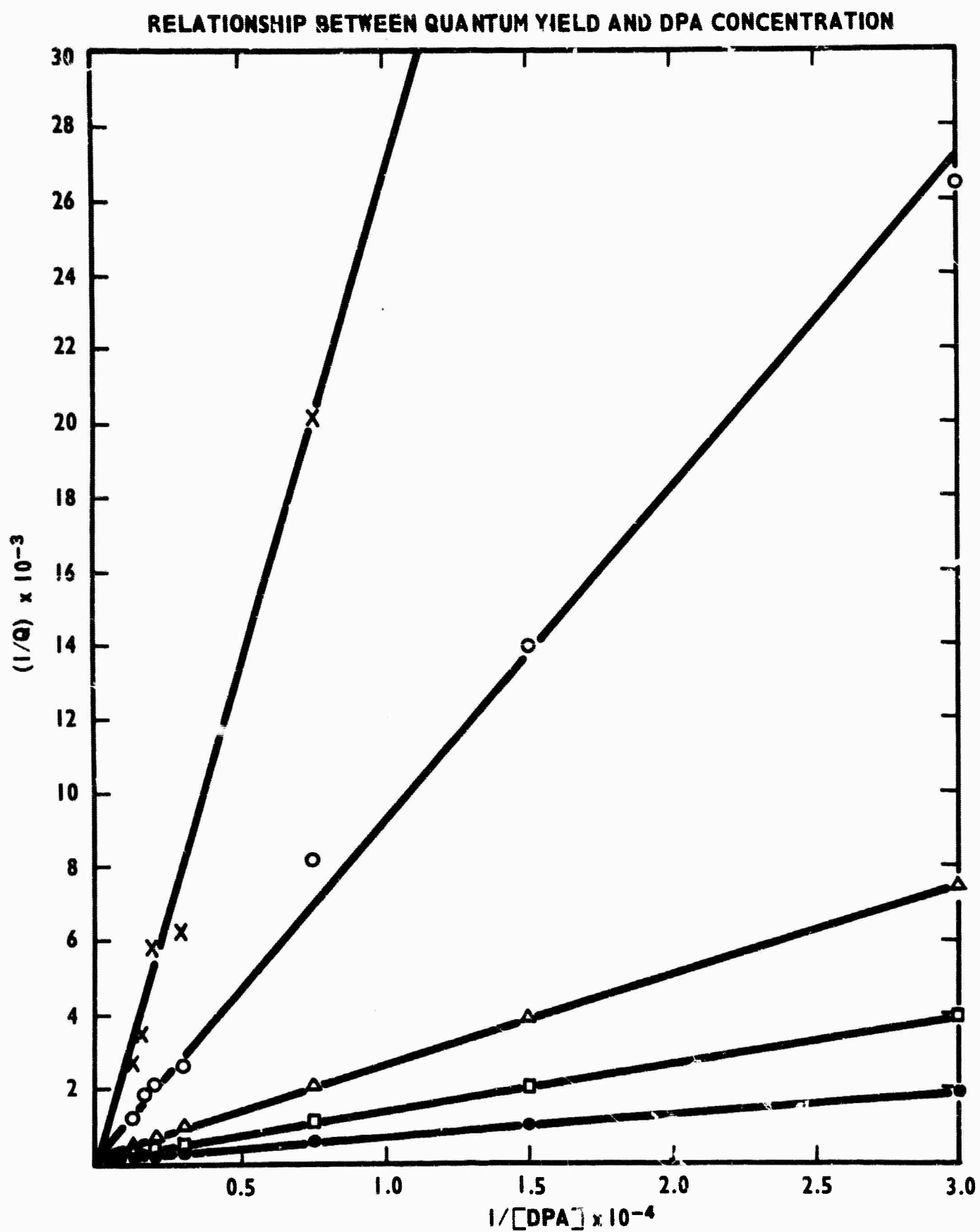
$$(a) \quad 1/Q = \frac{1}{K} \left(1 + \frac{k_6}{k_4[H_2O_2]} \right) \left(1 + \frac{k_8}{k_7[H_2O]} \right) \left(1 + \frac{k_{10}}{k_9[R\cdot][F]} \right)$$

In equation (a), Q is the quantum yield, K is a constant determined by the fluorescence quantum yield of the emitter and by the yield of excited fluorescer in step (9), $[R\cdot]$ is the steady state concentration of chain carrying free radicals, and $[F]$ is the fluorescer concentration. This equation permits several tests of the proposed mechanism in terms of the experimental data.

In experiments carried out with constant hydrogen peroxide and water concentrations, a linear plot of $1/Q$ vs. $1/[F]$ would be expected. Moreover, the slopes and intercepts of such linear plots should decrease as the hydrogen peroxide and water concentrations increase. Data reported previously⁷ is plotted in Figure 2, where it is seen that the predicted relationships are found.

In experiments carried out with constant water and fluorescer concentrations, a linear plot of $1/Q$ vs. $1/[H_2O_2]$ would be expected. Moreover, the slopes of such plots should decrease as the steady state concentration of free radicals increases. The data of Table III is plotted accordingly in Figure 3, where it is seen that the predicted relationships are found³¹. Equation (a) also indicates that the slopes of $1/Q$ vs. $1/[H_2O_2]$ plots should decrease with increasing water concentration. Data previously reported⁸ is plotted in Figure 4, where it is seen that the expected relationship is found.

Figure 2



NOTES TO FIGURE 2

• • • $[H_2O_2] = 20 \times 10^{-2} \underline{M}$

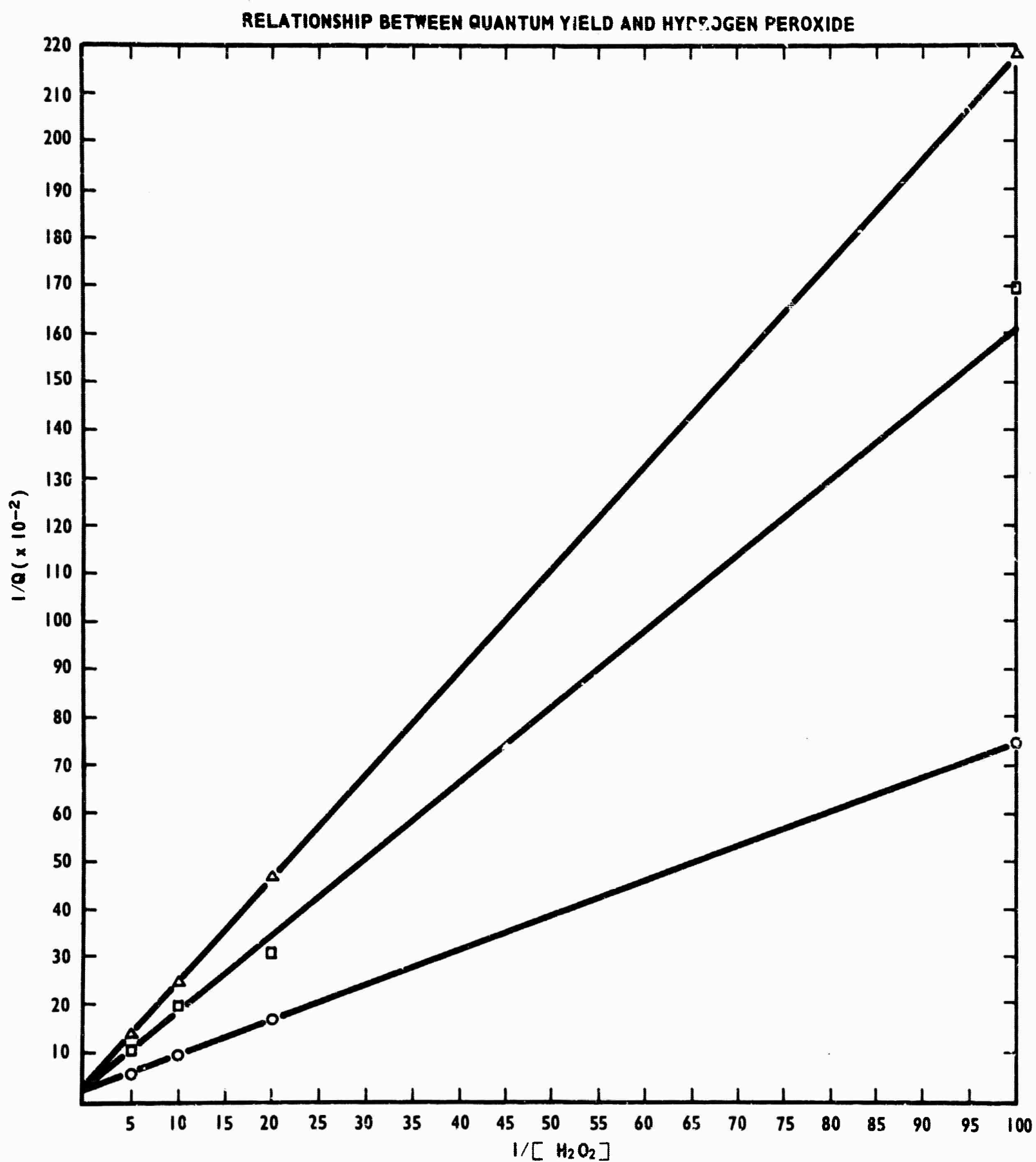
□ □ □ $[H_2O_2] = 10 \times 10^{-2} \underline{M}$

△ △ △ $[H_2O_2] = 5 \times 10^{-2} \underline{M}$


⊙ ⊙ ⊙ $[H_2O_2] = 2.0 \times 10^{-2} \underline{M}$

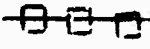
× × × $[H_2O_2] = 1.0 \times 10^{-2} \underline{M}$

Figure 3



NOTES TO FIGURE 3

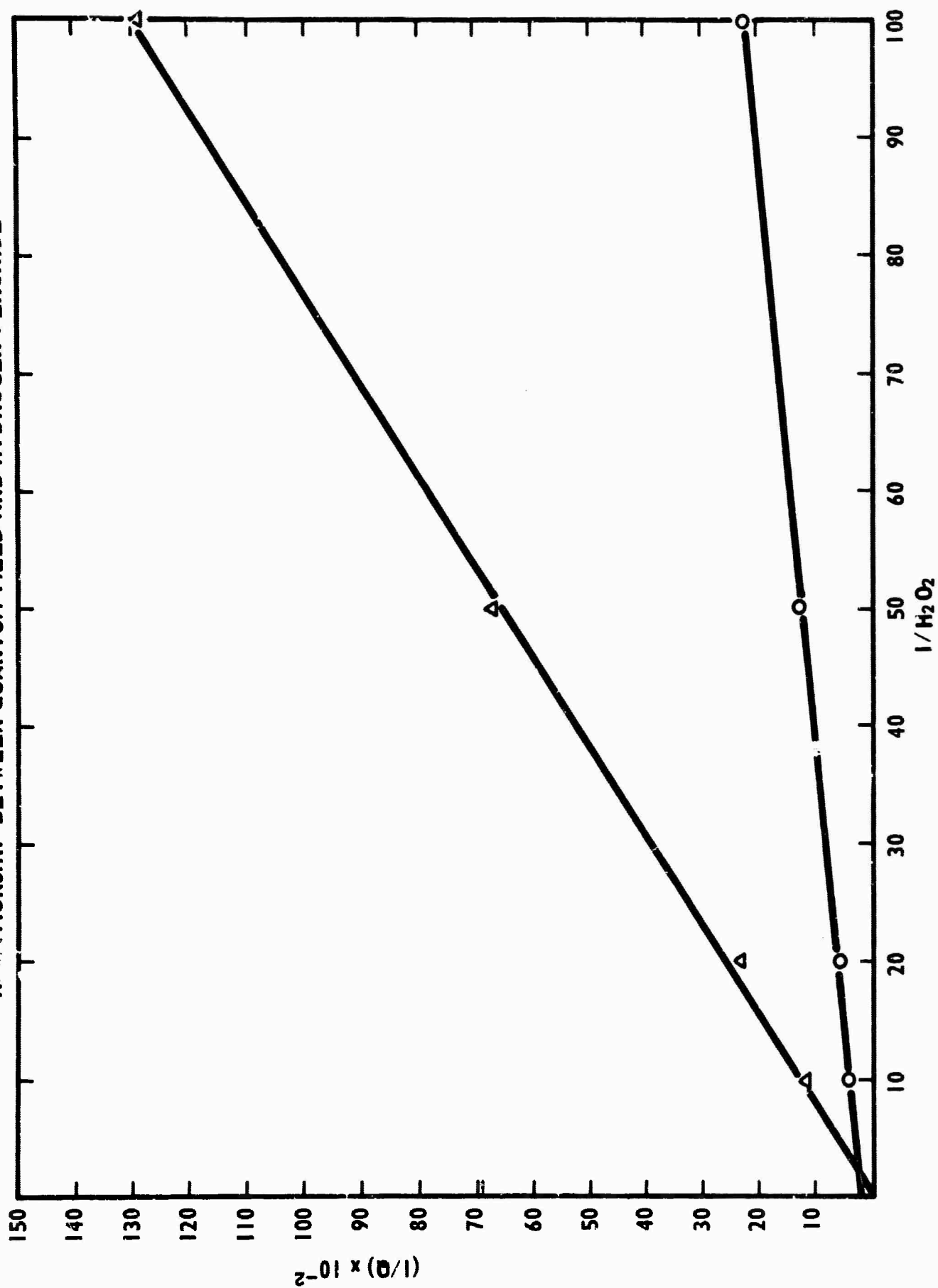
 Uninhibited Reaction.

 Styrene Inhibition.

 DTBMP Inhibition.

Data from Table III.

Figure 4
RELATIONSHIP BETWEEN QUANTUM YIELD AND HYDROGEN PEROXIDE



NOTES TO FIGURE 4

~~○ ○ ○~~ System Contained 3.4×10^{-2} M water

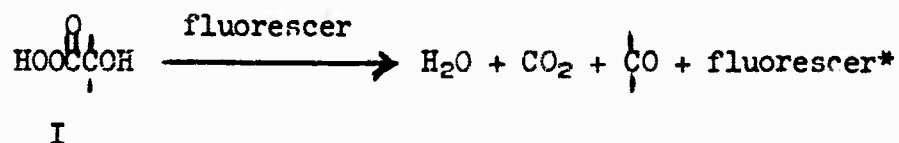
~~△ △ △~~ System Contained $\sim 1 \times 10^{-2}$ M water

In experiments carried out with constant hydrogen peroxide, water, and fluorescer concentrations, a linear plot of $1/Q$ vs. [inhibitor] would be expected from relationships (a) and (b).

$$(b) \quad [R\cdot] = \frac{\text{Rate of radical formation (R)}}{k(\text{inhib.}) [\text{inhibitor}]}$$

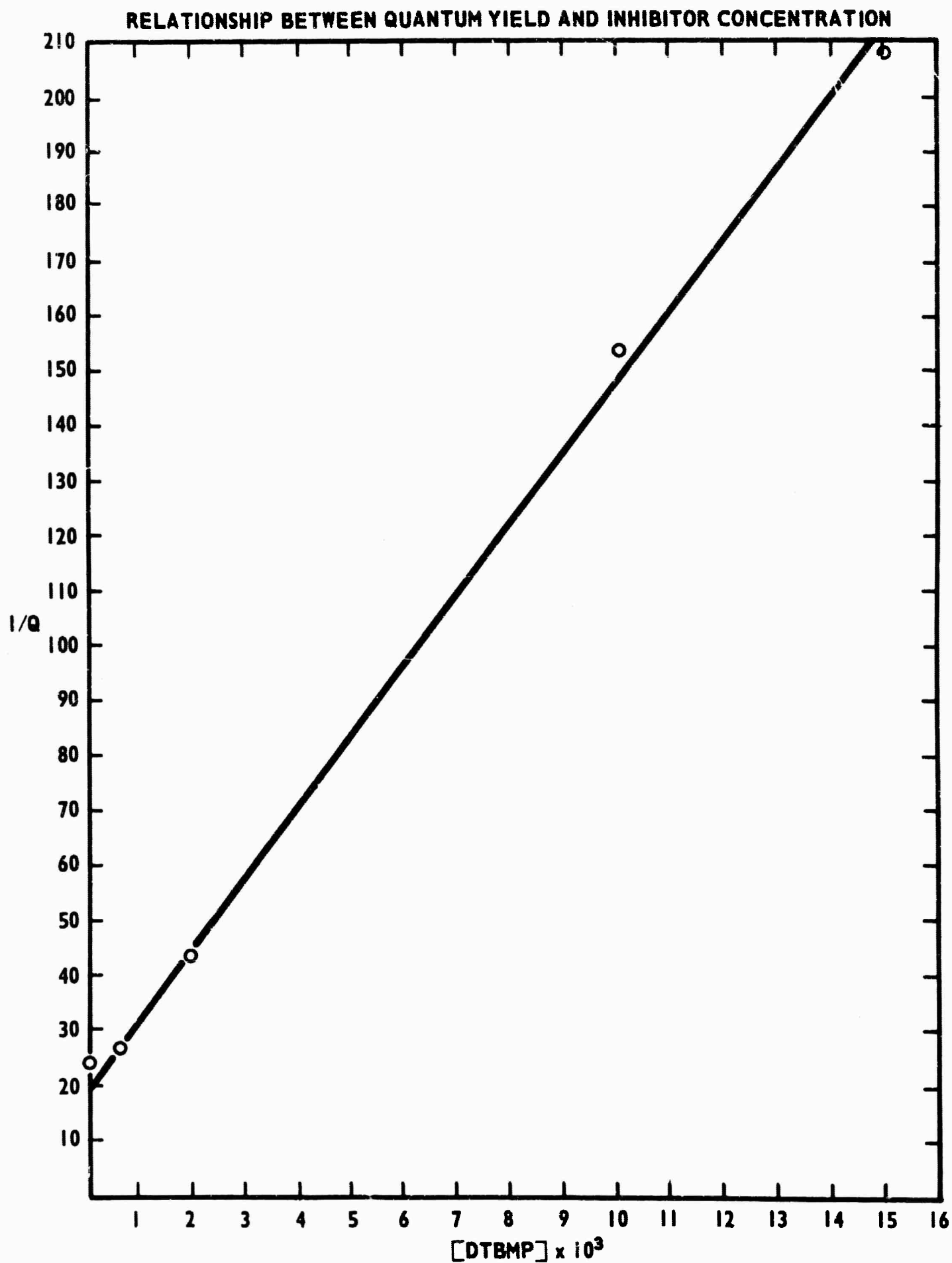
Equation (b) is only approximate since its derivation by the steady state assumption ignores termination steps not involving the inhibitor. Nevertheless, a reasonable linear plot of $1/Q$ vs. [inhibitor] is obtained from the data in Table II, as indicated in Figure 5.

The mechanism in Chart A indicates that decomposition of mono-peroxyoxalic acid uniquely provides the energy required to provide the excited state of the fluorescer. The assignment of step (9) to this key chemiluminescent role is in agreement with related work which has demonstrated chemiluminescence involving decomposition of a number of related peroxides^{2,3,4,5,6,7,8} (structure I).

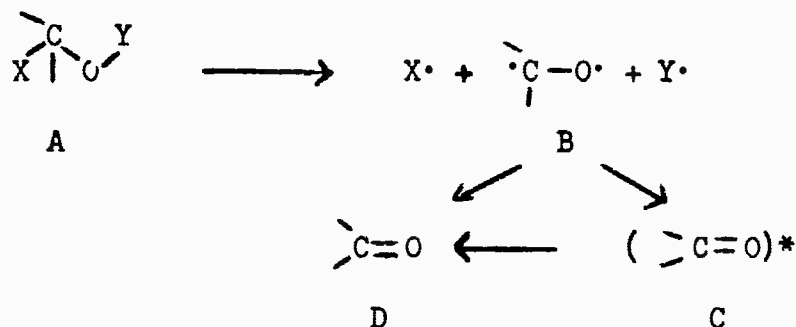


The chemiluminescent character of peroxides I, can be accounted for in terms of their ability to undergo concerted multiple bond cleavage decomposition³² where the simultaneous formation of several stable product molecules accommodates the synchronous release of the substantial energy required for excitation⁷.

Figure 5



Moreover, the formation of new carbonyl groups in such a process suggests a possible pathway for the conversion of chemical energy to electronic excitation energy.



The overall process from (A) to (D) clearly requires major electron reorganization and orbital rehybridization where electrons previously unpaired and in separate orbitals become paired. Providing sufficient energy is available, the transition state B might well retain the unpaired electron character, and this would require one of the unpaired electrons to be in an antibonding orbital corresponding to excited state (C). Formation of an excited state might also be facilitated by the conformational changes required between A and D. Thus excited singlet carbon dioxide has been shown to have a non-linear structure³³ and transition state B derived from non-linear A might be expected to be non-planar. Indeed, recent work by Bartlett has demonstrated that an alkyl radical formed by peroxyester decomposition can retain its original non-planar conformation for a short period.³⁴ Formation of C from A, of course, would be essentially synchronous with decomposition.

EXPERIMENTAL

Materials

Solvents. - Anhydrous ether (Mallinckrodt Reagent Grade) was further dried by passage through a 30 cm. neutral alumina column³⁵, or by distillation over lithium aluminum hydride under argon. Dimethylphthalate (Eastman) was distilled over lithium aluminum hydride. Residual water was estimated by the Karl Fischer method³⁶.

Oxalyl Chloride. - (Aldrich) was distilled through a 10 x 1 cm. Vigreux column under argon to obtain a fraction, b.p. 64° (1 atm.) (Lit.²², b.p., 63.5-64° (763 mm.)). Standard solutions of oxalyl chloride in ether or dimethylphthalate (1.11×10^{-1} M to 1.50×10^{-1} M) were analyzed gravimetrically by conversion to oxanilide with excess aniline. This reaction was shown to be quantitative in preliminary large scale experiments.

Anhydrous Hydrogen Peroxide in ether was prepared from 98% hydrogen peroxide (Becco Chemical Division, FMC Corp.) dissolved in ether to a concentration of 25%, and dried by shaking 16 hours with excess anhydrous magnesium sulfate³⁷. Water estimation of the dried solution by infrared analysis at 1640 cm.^{-1} indicated that residual water was below 2.9×10^{-2} M. Standard solutions of hydrogen peroxide (0.758 M to 1.65 M) were prepared from this solution and anhydrous ether and were analyzed iodometrically³⁸. Anhydrous hydrogen peroxide solutions in dimethylphthalate were prepared similarly.

9,10-Diphenylanthracene (DPA) (Aldrich) was recrystallized from abs. ethanol-chloroform to obtain material, m.p. 250-251° (Lit.³⁹, m.p., 250-251°).

2,6-Di-t-butyl-4-methylphenol (Koppers Co., Inc.) was sublimed in vacuo to obtain material melting at 69-70° (Lit.¹⁸, m.p. 69-70°).

Other materials were obtained from commercial sources and were recrystallized or redistilled before use.

Infrared Analyses of Oxalyl Chloride-Hydrogen Peroxide Reaction

Mixtures. - Aliquots of 1.5×10^{-1} molar oxalyl chloride and hydrogen peroxide solutions in ether were mixed rapidly and transferred to a 0.25 mm. infrared cell. Absorption bands at 1790 cm^{-1} and 750 cm^{-1} corresponding respectively to carbonyl and chlorocarbonyl were determined as a function of time at 25°. Typical results are shown in Figure 1

Determinations of Light Intensities, Spectra, and Quantum Yields

Instrumentation. - A combination spectroradiometer-fluorimeter, designed and calibrated under the direction of Dr. R. C. Hirt, has been described elsewhere in detail^{1,2}. The instrument consisted of a Bausch and Lomb grating monochromator (Model 33-86-25), an Aminco photomultiplier power supply and amplifier and a IP21 photomultiplier tube. The entrance and exit slits of the monochromator were fixed at 1.34 mm. and 0.75 mm. For fluorescence measurements, the instrument was equipped with a General Electric F4T 5/BLB fluorescent tube, mounted to provide frontside excitation of the sample. The amplifier output was fed to a Brown variable speed Electronik recorder or to a Leeds and Northrup integrating recorder for tracking spectral and intensity decay curves. The instrument was used without change for both fluorescence and chemiluminescence measurements. The liquid sample cell was

a 10.0 mm. thick, 22 mm. diameter cylindrical quartz cuvette of 3.0 ml. capacity. The instrument was calibrated using a National Bureau of Standards tungsten lamp, operated at a color temperature of 2864 °K, and the accepted fluorescence yield (0.55) for 1×10^{-3} M quinine sulfate⁴⁰ in 0.1 N H₂SO₄ according to standard procedures^{41,42}. The absolute intensity of exciting light incident on the cuvette was determined by ferrioxalate actinometry⁴³; the fraction of incident light absorbed in fluorescence experiments was calculated from the emission spectrum of the exciting light and from absorbance data determined with a Cary Model 14 spectrophotometer.

Calculation of Fluorescence and Chemiluminescence Quantum Yields -

Fluorescence quantum yields were calculated from the formula

$$Q_{Fl} = \frac{I_{\text{emission}}}{I_{\text{absorbed}}} = \frac{aa' \left(\int_{\lambda_1}^{\lambda_2} b_{\lambda} I_{\lambda} d\lambda \right)}{I_{\text{absorbed}}} = \frac{\int_{\lambda_1}^{\lambda_2} c_{\lambda} I_{\lambda} d\lambda}{I_{\text{absorbed}}}$$

where I_{λ} is the observed intensity as a function of wavelength λ ; b_{λ} is the wavelength sensitivity calibration factor for I_{λ} provided by the standard lamp; a is the reciprocal of the fraction of emitted light reaching the detector and a' is the conversion factor to absolute units, where aa' is determined by reference to quinine sulfate; c_{λ} is the product $aa'b_{\lambda}$. Since the instrument is unchanged for chemiluminescence measurements the factors c_{λ} are unchanged, permitting the determination of absolute chemiluminescence quantum yields.

Fluorescence quantum yields in deoxygenated solutions measured with the instrument agreed well with literature values: fluorescein in 0.1 M aqueous K_2CO_3 , 0.88 (lit. ⁴⁴, 0.92); eosin in 0.1 N aqueous NaOH, 0.17 (lit. ⁴⁵, 0.15, 0.23⁴¹) rhodamine B in ethanol, 0.92 (lit. ⁴⁴, 0.97); anthracene in ethanol, 0.25 (lit. ⁴⁶, 0.27); 9,10-diphenylanthracene in benzene, 0.84 (lit. ⁴⁶, 0.84).

The chemiluminescence quantum yields in Einsteins mole⁻¹ were calculated from the equation:

$$Q.Y. = \frac{\left(\int_0^\infty C_{\lambda'} I_{\lambda'} dT \right) \left(\frac{\int_{\lambda_1}^{\lambda_2} C_{\lambda} I_{\lambda}^T d\lambda}{C_{\lambda'} I_{\lambda'}^T} \right)}{3.0 \times 10^{-3} [\text{oxalyl chloride}] 6.02 \times 10^{23}}$$

The first product term in the numerator corresponds to the area of the corrected intensity vs. time decay plot at observed wavelength λ' , where $I_{\lambda'}$ is the observed intensity and $C_{\lambda'}$ is the instrument calibration factor for λ' . This term was measured graphically. The second product term in the numerator corresponds to the unit spectral area at time T. The spectral distribution and therefore the unit spectral area did not change appreciably during an experiment so that this was a constant factor for an experiment. This term can be calculated graphically from the area of a plot of $\frac{C_{\lambda} I_{\lambda}^T}{C_{\lambda'} I_{\lambda'}^T}$ vs. λ , but was actually determined with a Burroughs Datatron 205 Computer, programmed with the calibration data.

Procedure for Chemiluminescence Experiments. - The light measurement experiments were carried out by combining appropriate aliquots of standardized stock solutions of hydrogen peroxide, DPA and water in ether or dimethylphthalate with appropriate aliquots of solvent in a 3.0 ml. magnetically-stirred cylindrical cuvette attached to the radiometer. The stirrer was positioned vertically against the rear, flat side of the cuvette and provided efficient, rapid mixing. The shutter to the radiometer was opened, the recorder was started, and an aliquot of standardized oxalyl chloride was injected from an all-glass syringe. The intensity of emission of a 5 mμ-wide wavelength segment, usually selected at the spectral maximum, was recorded as a function of time from the point of oxalyl chloride injection. Spectral distributions were determined for representative experiments at several times during a single experiment. The time required for spectral scan was short relative to the intensity decay rate, however, the intensities were corrected for intensity decay. The spectral distributions did not change with time during an experiment under the conditions studied. Corrections of the spectra for reabsorption of emitted light was not necessary with DPA concentrations below 1×10^{-3} M; at 1×10^{-3} M, however, minor reabsorption was noted as a relative loss of intensity at short wavelength. The experiments were not thermostated but were run at room temperature, 25°C., which was constant within one degree. Exotherms were not observed at the low reactant concentrations used in several experiments where the temperature was followed with a thermocouple.

SECTION II

Chemiluminescence from Oxalic Acid Derivatives

Introduction - An extensive mechanistic investigation of the oxalyl chloride, hydrogen peroxide, fluorescer chemiluminescent reaction carried out during this program (see Section I) has indicated that the decomposition of monoperoxyoxalic acid in the presence of a fluorescer is a powerful source of chemiluminescent emission. This conclusion, which was unexpected in terms of the published literature, has encouraged us to investigate other reactions which, under appropriate conditions, might provide monoperoxyoxalic acid and thus provide new chemiluminescent systems.

Chemiluminescent systems previously available have serious defects barring broad use for practical lighting. These defects include low quantum yields, short lifetimes, and inconvenient operating characteristics. Thus, while the oxalyl chloride, hydrogen peroxide, fluorescer chemiluminescent system as modified in these laboratories is substantially more efficient than previously known chemiluminescent systems, its short lifetime makes it unsuitable for broad practical use. It is clear, however, that a reaction providing monoperoxyoxalic acid by a slow reaction process would provide a long-lived chemiluminescent system, in spite of the short lifetime of monoperoxyoxalic acid, itself. A search for such reactions has been underway in this program for some time. Preliminary results have encouraged us to concentrate a substantial effort on this approach.

Radiation Capacities

In view of the high quantum yields now available from oxalic anhydride and ester chemiluminescent systems it has become desirable to define a term for the total radiant energy emitted by a chemiluminescent system over its radiative lifetime. We thus define the "radiation capacity" of a chemiluminescent system by Equation (1).

$$(1) \quad R = \int_{T=0}^{T=\infty} I_E dT/V$$

In Equation (1), R is the radiation capacity in Einsteins (mole quanta) liter⁻¹, T is time in seconds, I_E is the chemiluminescent intensity in einsteins sec.⁻¹, and V is the volume of the chemiluminescent system in liters.

The radiation capacity is thus a fundamental criterion for practical chemical lighting. A system where R is below some specified value cannot be made to provide the volume of light required to meet the intensity and lifetime requirements for a given application. [A second criterion for practical chemical lighting, the "light capacity", which takes into account the variation of the eye's sensitivity with radiation wavelengths and the spectral distribution of emission will be defined and discussed when appropriate in a forthcoming report.]

The factors which determine the radiation capacity of a system are illustrated by Equation (2).

$$(2) \quad R = QM$$

In Equation (2), Q is the quantum yield in Einsteins mole⁻¹ and M is the concentration of limiting reactant in moles liter⁻¹. It is thus evident that the radiation capacity depends on the concentration of luminant, M as well as

the quantum yield, and that high radiation capacities require high quantum yields at high luminant concentrations. Radiation capacities for current experimental systems are reported in the following sections. A radiation capacity of 7.5×10^{-4} einsteins liter⁻¹ is considered to be within a practical range, provided the spectral distribution is of normal shape and lies predominantly within the 500-600 mμ spectral region.

Mixed Oxalic Anhydrides

In previous reports we have described a new class of chemiluminescent reactions based on reactions of carboxylic acid-oxalic acid anhydrides with hydrogen peroxide in the presence of a fluorescer^{7,8}. In the last report we provided preliminary data on the synthesis, stability and chemiluminescence of several oxalic anhydrides, and indicated in particular that bistritylacetic-oxalic anhydride was substantially superior in chemiluminescence quantum efficiency to any previously known chemical system. Results of current studies of oxalic anhydride chemiluminescence are summarized below.

Bistritylacetic Oxalic Anhydride (TPAO)

Since the radiation and visual light capacities of chemiluminescent systems are a function of the luminant concentration as well as quantum yield, we have begun a series of experiments to determine the effect of luminant concentration on quantum yield and radiation capacity in the TPAO-hydrogen peroxide-DPA chemiluminescent system.

The choice of solvents for high concentration experiments was found to be limited by the low solubility of TPAO in most organic solvents as well as by the rapid reaction of TPAO with solvents containing active

hydrogen. In preliminary solubility determinations, however, it was found that TPAO was soluble in benzene to the extent of about $0.1 \text{ mole liter}^{-1}$, a solubility four to five times greater than that obtained in dimethylphthalate or 1,2-dimethoxyethane. Moreover, 0.078 M solutions of TPAO in anhydrous benzene appear to be reasonably stable with little deterioration observed over a two week period at room temperature (see Table VII). Although hydrogen peroxide is essentially insoluble in benzene, it was found that solvent mixtures of benzene and dimethylphthalate provided sufficient solubility for both TPAO and hydrogen peroxide to permit examination of TPAO concentrations up to at least 5×10^{-2} molar under homogeneous conditions.

Results from a series of experiments carried out by combining aliquots of 0.078 M solutions of TPAO in benzene and 1.5 M solutions of hydrogen peroxide in dimethylphthalate (DMP) with benzene containing 9,10-diphenylanthracene (DPA) are summarized in Table I. It is evident from the table that under the conditions studied the quantum yield is substantially lower at high TPAO concentration, but that the radiation capacity is higher. The quantum yield, however, is strongly influenced by the condition of reaction as indicated below and additional studies are needed to determine the optimum light capacity.

An experiment was carried out to explore the possibility of improving the quantum yield by the addition of water. Enough water was added to the chemiluminescent system to form a two phase mixture. Thorough mixing was assured by an efficient magnetic stirrer. As indicated in Table I the experiment showed a substantial increase of quantum yield. The added water also eliminated the induction period and increased the emission lifetime.

TABLE I

Chemiluminescence from the Bis(tribenzylacetic Oxalic Anhydride (TBAO))-Hydrogen Peroxide-DPA Systems in Benzene-Dimethylphthalate^a

TBAO (mole l. ⁻¹)	H ₂ O ₂ (mole l. ⁻¹)	H ₂ O ₂ /TBAO	Solvent % DMP by Volume	t _{ind} (min.)	b	t _{max} ^c (min.)	t _{1/2} ^d (min.)	I _{max} ^e (foot-lambert)	Quantum Yield (Einsteins mole ⁻¹ l. ⁻¹)	Radiation Capacity (Einsteins l. ⁻¹)
5.2 x 10 ⁻³	0.075	14.4	25.7	10	10	240.0	310	0.006	4.62 x 10 ⁻²	2.40 x 10 ⁻⁴
5.2 x 10 ⁻³	0.075	14.4	25.7	30	30	180.0	360	0.008	4.12 x 10 ⁻²	2.14 x 10 ⁻⁴
4.94 x 10 ⁻²	0.045	0.91	25.7	8	8	28.0	155	0.036	0.654 x 10 ⁻²	3.23 x 10 ⁻⁴
4.94 x 10 ⁻²	0.15	3.04	30.0	9	9	27.0	64	0.047	0.506 x 10 ⁻²	2.50 x 10 ⁻⁴
4.94 x 10 ⁻²	0.25	5.06	40	12	12	21.5	7.5	0.109	0.199 x 10 ⁻²	0.98 x 10 ⁻⁴
4.94 x 10 ^{-2f}	0.25	5.06	40	None	None	2.0	10.5	0.69	1.23 x 10 ⁻²	6.06 x 10 ⁻⁴
4.94 x 10 ^{-2g}	0.315	6.36	25.7	30	30	100	300	0.033	1.20 x 10 ⁻²	5.92 x 10 ⁻⁴
4.94 x 10 ⁻²	4.0	20.75	30	9	9	21.5	14	0.03	0.107 x 10 ⁻²	0.53 x 10 ⁻⁴

a) The DPA concentration was 1 x 10⁻³ mole l.⁻¹.

b) Induction period during which little emission was observed.

c) The time required to reach maximum light intensity.

d) The time required for the light intensity to decrease to one quarter of its maximum value.

e) Maximum value of the emitted light intensity for a 1 cm. thick sample.

f) Five drops (approximately 1.8 mole l.⁻¹) of water were added after 1.5 minutes to give a two phase reaction mixture. However, the water was well dispersed due to the excellent agitation by means of a magnetic stirrer.g) The hydrogen peroxide was added periodically in seven 1.35 x 10⁻⁴ mole portions (13.5 ml. of molar hydrogen peroxide in DMP) to the 3 ml. reaction mixture. After the chemiluminescent light intensity resulting from the previous peroxide portion decreased to one half of its maximum value, a new portion of peroxide was added. The experiment was discontinued after the seventh addition because of lack of time and not because of the exhaustion of chemiluminescent light.

Decreasing initial hydrogen peroxide concentrations are shown in Table I to result in increasing quantum yields at high TPAO concentration. Furthermore, this effect persists even at low hydrogen peroxide concentrations when less than one molecular equivalent hydrogen peroxide to TPAO is present. However, substantial improvement of the quantum yield is also observed when large amounts of hydrogen peroxide are added in small portions periodically, pausing long enough between additions to have most of the chemiluminescence discharged before the next portion of hydrogen peroxide is added.

It is possible that the observed increase in quantum yield resulting from added water in a two phase system and that observed from hydrogen peroxide added in small portions are closely related. Earlier reports⁸ indicated that addition of small amounts of water, soluble in DMP, or larger amounts of water, leading to a separate phase which is not kept in suspension by mixing, do not substantially affect the quantum yield. However, when enough water is added to form a two phase system, kept thoroughly mixed by good agitation, the quantum yield is increased substantially. Probably, the hydrogen peroxide is distributed between the two phases and released by the aqueous phase slowly thereby maintaining a low hydrogen peroxide concentration in the organic layer at all times. Although the distribution coefficient is not known precisely for the system used, the aqueous phase must hold many times more hydrogen peroxide than the benzene-DMP layer, since the aqueous phase of the benzene-water system is reported to hold 200 times more hydrogen peroxide than the benzene layer⁴⁷.

The high quantum yields and radiation capacities demonstrated in Table I make the TPAO-hydrogen peroxide-fluorescer system one of the most promising chemiluminescent reactions. Both the quantum yield and radiation capacity may be subject to further improvement by the proper choice of reaction conditions. A major difficulty with this system, however, arises from a marked reactivity of TPAO toward hydrolysis and its base catalyzed decomposition to triphenylacetic anhydride. Although both of these problems may be overcome, they interfere with the preparation, easy handling and easy storage of TPAO.

TPAO is currently prepared by the reaction of potassium triphenyl acetate, suspended in benzene, with oxalyl chloride⁷. Yields are low because of the insolubility of the potassium salt and the sensitivity of TPAO to hydrolysis.

Two alternative synthetic procedures were examined in an effort to improve yields. In the first attempt, triphenylacetic acid was reacted with oxalyl chloride in the presence of triethylenediamine. It was hoped that this sterically hindered amine would react with the hydrogen chloride by-product but not catalyze the decomposition of TPAO. However, the only anhydride obtained was triphenyl acetic anhydride, the product of base catalyzed decomposition of TPAO.

Triphenylacetylchloride fails to react with potassium oxalate because of the poor solubility of the oxalate in most organic solvents. In a second attempt to improve the synthetic method, the commercially available benzoyl chloride, used as a model compound, was reacted with freshly prepared tetrabutylammonium oxalate in benzene. However, benzoic anhydride was the product.

Substituted Benzoic Oxalic Anhydrides

Methoxy and nitro substituted benzoic oxalic anhydrides are being prepared to test the possibility of improving the efficiency of the weakly chemiluminescent benzoic oxalic anhydride by structural modification. The first compound prepared, 4-methoxy benzoic oxalic anhydride, gave a medium-strong chemiluminescent reaction with hydrogen peroxide in the presence of DPA, as indicated in Table II. This strong substituent effect of the methoxy group suggests that a proper choice of substituents should improve greatly the chemiluminescent properties of unsubstituted benzoic oxalic anhydride.

TABLE II

Qualitative Test of Chemiluminescence of Benzoic Oxalic Anhydride

<u>Test</u>	<u>4-Methoxybenzoic oxalic anhydride</u>	<u>Benzoic oxalic anhydride</u>
A	MS	None
B	MS	VW
C	MS	VW
D	S	M

FOOTNOTES FOR TABLE II

Tests:

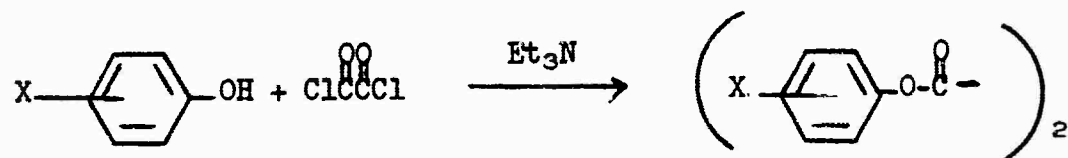
- Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of about 1 mg. DPA in 1,2-dimethoxyethane containing 5% water at 25°C. About 5 mg. Na_2O_2 is added immediately.
- Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of 1 mg. DPA and 0.2 ml. $\text{CH}_3\text{SO}_3\text{H}$ in 1,2-dimethoxyethane containing 5% water and maintained at 25°C. About 0.5 ml. 30% H_2O_2 is added immediately.
- Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of about 1 mg. DPA and 0.2 ml. anhydrous H_2O_2 in anhydrous 1,2-dimethoxyethane maintained at 25°C.
- Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. slurry of 1 mg. DPA, ~0.2 g. KOH (1 pellet) and 0.2 ml. anhydrous H_2C_2 in anhydrous 1,2-dimethoxyethane maintained at 25°C.

Oxalic Esters

A preliminary examination of oxalic esters for chemiluminescence in reactions with aqueous hydrogen peroxide in the presence of a fluorescer indicated that most such reactions provide only weak emission at best.⁷ Thus, weak emission was observed from reactions with several alkyl esters, and even under strongly alkaline conditions only a medium intensity emission was observed from a reaction with diphenyloxalate. Unwilling to abandon this approach, we have now examined a substantial number of aryl oxalic ester reactions and report below that certain esters can provide exceptional chemiluminescent intensities and efficiencies.

Preparation of Oxalic Esters


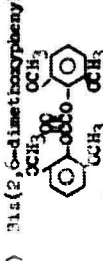

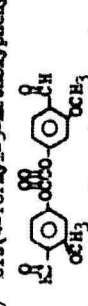


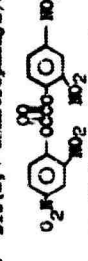
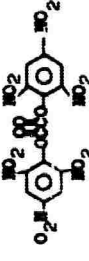
A series of oxalic esters (see Table III) has been prepared by the reaction of oxalyl chloride with the corresponding phenol in the presence of triethylamine.⁷



The preparation is straightforward and does not involve serious problems. Yields are acceptable in the case of most compounds but are subject to improvement.



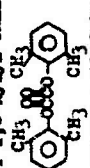




Oxalic esters proved to be much more stable to hydrolysis than mixed oxalic anhydrides, as expected. During the course of their preparation for example, the esters could be washed with water to remove the triethylamine hydrochloride by-product. Only the 2,4-dinitrophenyl and o-phenylene oxalate required special care and immediate drying to prevent extensive hydrolysis.

TABLE III

Compound	Yield	M.P.	Lit. M.P.	Analytical Data	Infrared Data - C=O Stretching Frequencies (cm. ⁻¹)	
					Solids in Nujol	Solution in Carbon Tetrachloride
1) Bis(p-acetylphenyl)oxalate 	61%	269-272°C (decomp.)		Calcd. for C ₁₈ H ₁₄ O ₆ : C, 66.25; H, 4.32. Found: C, 66.13; H, 4.84.	1765	1792 1772 Cis Trans
2) Bis(2,6-dimethoxyphenyl)oxalate 	53%	214-217°C		Calcd. for C ₁₈ H ₁₈ O ₈ : C, 59.66; H, 5.01. Found: C, 60.22; H, 5.31	1765	1795 1767
3) Bis(4-biphenyl)oxalate 	62%	236-237.5°C		Calcd. for C ₂₆ H ₁₈ O ₄ : C, 79.17; H, 4.60. Found: C, 79.53; H, 5.03.	1762	1794 1767
4) Bis(4-formyl-3-methoxyphenyl)oxalate 	67%	206-209°C (decomp.)		Calcd. for C ₁₈ H ₁₄ O ₆ : C, 60.34; H, 3.94. Found: C, 60.11; H, 4.15	1770	1793 1775
5) Bis(p-methoxyphenyl)oxalate 	56%	157-159°C		Calcd. for C ₁₆ H ₁₄ O ₆ : C, 63.57; H, 4.67. Found: C, 63.84; H, 4.76	1765	1789 1766
6) Bis(p-nitrophenyl)oxalate 	66%	240-242°C (Ethyl acetate)	261-265°C ⁴⁸ (dioxane)	Calcd. for C ₁₄ H ₈ O ₈ : C, 50.61; H, 2.43; N, 8.43. Found: C, 50.30; 50.64; H, 2.78, 2.87; N, 8.40.	1776	1797 (1775 solid?)
7) Bis(2,4-dinitrophenyl)oxalate 	39%	192-194°C		Calcd. for C ₁₄ H ₆ O ₁₂ N ₄ : C, 39.82; H, 1.43; N, 13.27. Found: C, 39.97; H, 1.65; N, 13.47.	1790	1812 1789
8) Bis(2,4,6-trinitrophenyl)oxalate 	38%	198-201°C (decomp.)		Calcd. for C ₁₄ H ₃ O ₁₅ N ₆ : C, 32.82; H, 0.79; N, 16.41. Found: C, 33.01; H, 1.17; N, 15.99	1812	1813

(Table III continued)

TABLE III (continued)

Compound	Yield	M.P.	Lit. M.P.	Analytical Data	Infrared Data - C=O Stretching Frequencies (cm. ⁻¹)	
					Solids in Methyl	Solution in Carbon Tetrachloride
9) <i>p</i> -Phenylene oxalate 	24%	187-189°C		Calcd. for C ₈ H ₄ O ₄ : C, 58.55; H, 2.46. Found: C, 58.38; H, 2.76	1810 and 1778 (in plane)	1788
10) Diphenacyl oxalate 	12%	115.5-117°C		Calcd. for C ₁₈ H ₁₄ O ₆ : C, 66.25; H, 4.34. Found: C, 66.10; H, 4.47	1752	1764
11) Di-2,6-pyridyl oxalate 	15%	126-126.5°C		Calcd. for C ₁₈ H ₁₀ O ₄ : C, 72.46; H, 6.08. Found: C, 71.83; H, 6.11	1752	1760
12) Diphenylmethylphenyl oxalate 	33%	76.5-78°C		Calcd. for C ₂₁ H ₁₆ O ₄ : C, 75.89; H, 4.85. Found: C, 75.99; H, 4.95	1740, 1778	1740, 1778 1786, 1757
13) Bis(p-cyanophenyl)oxalate 	68%	216-218°C		Calcd. for C ₁₆ H ₈ O ₄ : C, 65.75; H, 2.76; N, 9.59. Found: C, 65.65; H, 2.91; N, 9.96	1762	1774
14) Di-2-naphthyl oxalate 	60%	187-189°C	188-189°C ⁴⁹	Calcd. for C ₂₂ H ₁₄ O ₄ : C, 77.18; H, 4.12. Found: C, 76.92; H, 4.12.	1769	1793 1771
15) Phenyl oxalyl chloride 		53-54°C	57°C ⁵⁴			

Differential thermal analysis and thermal gravimetric analysis measurements indicate that 4-nitrophenyl oxalate and 2,4-dinitrophenyl oxalate remain stable, up to 120°C and 200°C, respectively. Similar behavior is expected from most substituted phenyl oxalates. However, some decomposition of several of these esters was observed including that of the dinitro compound, on a few weeks storage at room temperature. But, these decompositions probably result from the unusual light sensitivity of phenol esters reported recently by D. H. R. Barton and coworkers.⁵⁰ Storage in a dark bottle or in a dark place should eliminate this problem. This will be investigated.

Chemiluminescent Properties of Oxalic Esters

Results of a qualitative examination of aryl oxalic esters for chemiluminescence on reaction with hydrogen peroxide in 1,2-dimethoxyethane solvent containing 9,10-diphenylanthracene are summarized in Table IV.

It is evident from the data in Table IV that chemiluminescence increases with the electron withdrawing character of the substituents. Electron releasing groups eliminate even the chemiluminescence of the unsubstituted phenyl oxalate. Substituent effects on chemiluminescent intensities parallel those observed for base catalyzed hydrolysis of phenyl acetate⁵¹ supporting the hypothesis that the first step of the chemiluminescence reaction consists of the reaction between hydrogen peroxide and the oxalic ester. Although the effect of substituents is established clearly, no quantitative correlation can be attempted yet between Hammett σ values and chemiluminescence because of the qualitative nature of the chemiluminescence data.

TABLE IV
Qualitative Chemiluminescence Test of Oxalic Esters

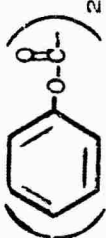

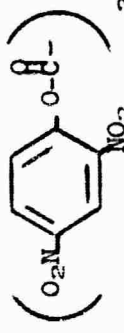
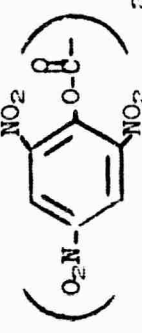
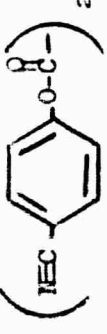
Compound	TESTS ^a						
	A (anhyd. H ₂ O ₂)	B (H ₂ O ₂ + KOH)	C (H ₂ O ₂ + H ₂ O)	D (H ₂ O ₂ + imidazole)	E (H ₂ O ₂ + H ₂ O + imidazole)	F (Na ₂ O ₂)	G (H ₂ O ₂ + H ₂ O ⁺)
	VW	M	W	W	VW	W	VW
	W	M	MS	MW	MS	W	W
	MS	S	M	None	--	W	MS
	M	MS	None	--	--	None	M/
	MW	M	M	--	--	VW	None

TABLE IV (continued)


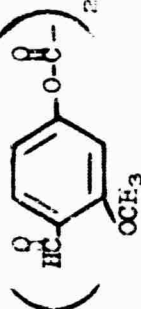
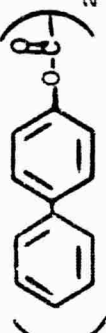

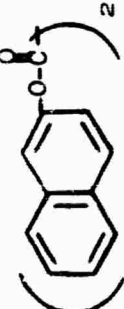

Compound	TESTS ^a						
	A (anhyd. H ₂ O ₂)	B (H ₂ O ₂ + KOH)	C (H ₂ O ₂ + H ₂ O)	D (H ₂ O ₂ + imidazole)	E (H ₂ O ₂ + H ₂ O + imidazole)	F (Na ₂ O ₂)	G (H ₂ O ₂ + H ₃ O ⁺)
	VW	M	None	W	W	None	W
	MW	MS	VW	M	MW	VW	VW
	VW	M	W	VW	VW	None	None
	W	W	W	W	W	None	None
	VW	VW	VW	--	--	VW	W
	VW	VW	None	--	--	None	None

Table IV continued

TABLE IV (continued)

Compound	TESTS ^a						
	A (anhyd. H ₂ O ₂)	B (H ₂ O ₂ + KOH)	C (H ₂ O ₂ + H ₂ O)	D (H ₂ O ₂ + imidazole)	E (H ₂ O ₂ + H ₂ O + imidazole)	F (Na ₂ O ₂)	G (H ₂ O ₂ + H ₃ O ⁺)
	None	None	VW	None	VW	None	None
	None	None	None	None	None	None	None
	None	None	None	None	None	None	None
	None	None	None	None	None	None	None
	None	W	VW	None	--	None	None
	None	None	None	None	--	None	None
	M	M	None	--	--	None	NE

NOTES TO TABLE IV

a) The tests were carried out as follows:

- A. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of about 1 mg. DPA and 0.2 ml. anhydrous H_2O_2 in anhydrous 1,2-dimethoxyethane maintained at 25°C.
- B. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. slurry of 1 mg. DPA, 0.2 g. KOH (1 pellet) and 0.2 ml. anhydrous H_2O_2 in anhydrous 1,2-dimethoxyethane maintained at 25°C.
- C. As test A except that approximately 0.1 ml. water was added prior to the addition of the compound being tested.
- D. As test A except that approximately 3 mg. imidazole was added to the solution prior to the addition of the compound being tested.
- E. As test D except that approximately 0.1 ml. water was added prior to the addition of the compound being tested.
- F. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of about 1 mg. DPA in 1,2-dimethoxyethane containing 5% water at 25°C. About 5 mg. Na_2O_2 is added immediately.
- G. Approximately 3-5 mg. of the compound to be tested is added to a 5 ml. solution of 1 mg. DPA and 0.2 ml. CH_3SO_3H in 1,2-dimethoxyethane containing 5% water and maintained at 25°C. About 0.5 ml. 30% H_2O_2 is added immediately.

Qualitative intensities are based on the oxalyl chloride, hydrogen peroxide reaction taken as strong (S). Other designations are M = medium; W = weak; VW = very weak, barely visible.

Attempts were made to catalyze the chemiluminescence reaction by imidazole (see Tests D and E in Table IV). Imidazole is known to catalyze the hydrolysis of phenol esters especially nitrophenol or thiophenol esters^{52,53}. However, only a very modest improvement of the chemiluminescence was observed at best. Steps subsequent to the initial ester-hydrogen peroxide reaction, however, may be effected adversely by imidazole.

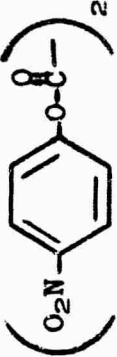
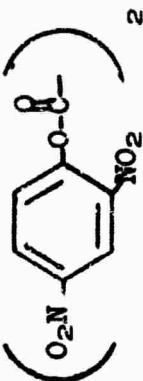
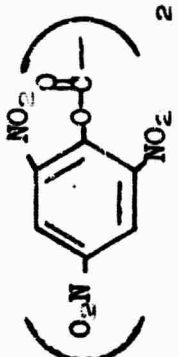
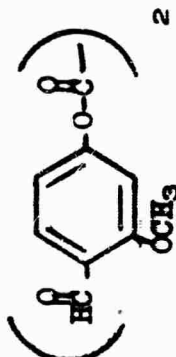
The most promising esters in Table IV are being examined quantitatively under a variety of conditions to provide efficiency and lifetime data required to optimize radiation capacities and to determine reaction condition effects that may have bearings on the mechanism of the reaction.

Most aryl oxalates are only poorly soluble in organic solvents, but a relatively high concentration of the reactant is required to achieve high chemiluminescent radiation capacity and light intensity at moderate quantum yields. Therefore, the solubility of several oxalic esters was determined first in a number of solvents found satisfactory for the chemiluminescent reaction. The results are given in Table V.

The solubilities at best were found to be only moderate. Other solvents considered either failed to dissolve hydrogen peroxide (e.g., anisole and carbon tetrachloride) or yielded only poor chemiluminescence (e.g., DMSO, hexamethylphosphoramide, chloroform, tetramethylurea). Dimethylphthalate was selected for the measurements because the non-hygroscopic nature of this solvent reduces complication by hydrolysis of the oxalic ester prior to the measurement.

TABLE V

Approximate Solubilities^a

<u>Solubilities in Solvents (mole l.⁻¹)</u>				
<u>Compound</u>	<u>Benzene</u>	<u>Dimethylphthalate</u>	<u>Bis 2,2'-dimethoxyethyl ether</u>	<u>Tetrahydrofuran</u>
	1.4 x 10 ⁻³		4 x 10 ⁻³	5 x 10 ⁻³
	5 x 10 ⁻³	2.8 x 10 ⁻²	4 x 10 ⁻²	4.7 x 10 ⁻²
		1 x 10 ⁻¹	1.9 x 10 ⁻¹	
		4.3 x 10 ⁻²	4.9 x 10 ⁻³	5.7 x 10 ⁻³

a) Solubilities were determined by the addition of small portions (0.2-0.3 ml.) of solvent to a test tube containing a known amount (~100 mg.) of the compound being stirred by a magnetic stirrer, until all the compound dissolved in approximately two hours.

Results obtained to date with 2,4-dinitrophenyl oxalate (DNPO) are summarized in Table VI.

The increase of DNPO concentration up to 1×10^{-2} mole l^{-1} decreases the quantum yield only moderately so that light intensities and radiation capacities are substantially increased. At concentration levels of 10^{-3} mole l^{-1} or below, the quantum yield is not affected by the DNPO concentration. However, under the conditions tested the intensity increases but lifetime decreases with increasing DNPO concentration.

Increasing hydrogen peroxide concentration lead to a moderate decrease of quantum yield and radiation capacity but to a pronounced decrease of light intensity and a noticeable increase of lifetime.

The addition of water up to a ninety fold excess of the DNPO present does not affect the quantum yield. However, increasing water concentration brings about a significant increase of light intensity and a corresponding shortening of lifetime.

On the basis of the demonstrated high quantum yield and high radiation capacity, the DNPO-hydrogen peroxide-fluorescer system appears to be very promising. This system lends itself readily to the regulation of light intensity and lifetime by the addition of water and hydrogen peroxide. Further cause for optimism lies in the fact that DNPO appears to be reasonably stable to both thermal decomposition and hydrolysis.

TABLE VI

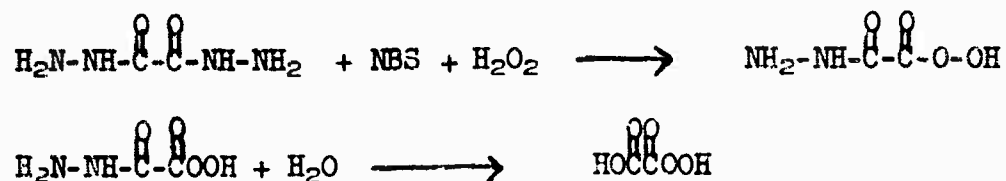
Chemiluminescence Data for the Bis-2,4-dinitrophenyl oxalate (DNPO) - Hydrogen Peroxide - DPA System in Dimethyl phthalate Solutions^a

$[DNPO]$ mole l. ⁻¹	$[H_2O_2]$ mole l. ⁻¹	$H_2O_2/DNPO$	$[H_2O]$ mole l. ⁻¹	Age of Ester Stock Solution in hrs.	$t_{I \max.}$ min.	$t_{1/4 \max.}$ min.	$I \max.$ ^d Foot Lambert	Quantum Yield Einstein mole ⁻¹	Radiation Capacity Einstein l. ⁻¹
0.69×10^{-4}	0.1	1124	--	0.75	27.0	48	0.002	13.9×10^{-2}	0.124×10^{-4}
1.11×10^{-3}	0.1	90	--	0	7.5	13	0.118	13.2×10^{-2}	1.47×10^{-4}
1.11×10^{-3}	0.1	90	--	3.5	6.0	11.5	0.121	12.2×10^{-2}	1.36×10^{-4}
1.11×10^{-3}	0.1	90	--	5.0	5.5	11.5	0.121	12.2×10^{-2}	1.36×10^{-4}
1.11×10^{-3}	0.1	90	--	26.0	11.5	30	0.028	10.2×10^{-2}	1.13×10^{-4}
1.11×10^{-3}	0.1	90	--	27.5	10.0	59	0.040	10.0×10^{-2}	1.11×10^{-4}
1.11×10^{-3}	0.1	90	--	49.0	8.0	23	0.052	10.5×10^{-2}	1.17×10^{-4}
1.11×10^{-3}	0.1	90	--	120.0	7.0	47	0.007	4.1×10^{-2}	0.46×10^{-4}
1.11×10^{-3}	0.01	9	--	4.5	0.3	6	0.312	12.3×10^{-2}	1.37×10^{-4}
1.11×10^{-3}	0.5	450	--	4.0	12.0	26	0.040	8.1×10^{-2}	0.90×10^{-4}
1.11×10^{-3}	0.1	90	0.5×10^{-2}	6.5	8.5	21	0.062	11.2×10^{-2}	1.24×10^{-4}
1.11×10^{-3}	0.1	90	2.5×10^{-2}	6.0	5.5	12	0.108	12.2×10^{-2}	1.36×10^{-4}
1.11×10^{-3}	0.1	90	10.0×10^{-2}	5.5	2.5	6	0.200	10.7×10^{-2}	1.13×10^{-4}
1×10^{-2}	0.1	10	--	1.25	0.1	4	3.05	7.4×10^{-2}	7.4×10^{-4}

^a DPA = 5×10^{-4} mole l.⁻¹^b $t_{I \max.}$ = time required to reach $I \max.$ ^c $t_{1/4 \max.}$ = time required for the light intensity to decrease to one quarter its maximum value.^d $I \max.$ = maximum value of emitted light intensity.

Chemiluminescence from Oxalic Dihydrazide

Professor Gilbert Stork suggested the possibility that oxalic acid hydrazide might undergo a chemiluminescent reaction with hydrogen peroxide and N-bromosuccinimide (NBS) in the presence of a fluorescer according to the following reaction scheme.



A brief moderate intensity chemiluminescence was indeed observed using either NBS or t-butylhypochlorite as oxidizing agent. Further experiments are required to estimate the scope of this reaction.

SECTION II

EXPERIMENTAL

Infrared Study of the Solution Stability of Triphenylacetic Oxalic Anhydride in Benzene

The experiment was carried out in a dry-box under an argon atmosphere. The benzene solvent employed in this study was dried over elemental sodium and distilled under an argon atmosphere. A Karl Fischer water analysis done on a sample of the solvent showed the presence of 0.01% water. All glassware used in this experiment was cleaned with chrome-sulfuric acid solution, washed with 2% aqueous ammonia and with distilled water, and dried in an oven at 110° for at least one hour.

A 0.078 M solution of triphenylacetic oxalic anhydride was prepared in the following manner. A 1.8938 g. sample of the anhydride was transferred to a tared 25 ml. volumetric flask. The benzene solvent was added, and after 20 minutes shaking, the undissolved material was collected, dried, and weighed on a tared sintered-glass filter to recover 0.6595 g. anhydride. The concentration of the solution was calculated to be 0.078 moles/liter. The anhydride solution was transferred to a serum-capped bottle. Samples of the solution were withdrawn periodically by the use of a syringe, and analyzed by infrared spectroscopy, measuring the absorbance of each sample at 1770 cm.⁻¹ in a cell 0.0105 cm. thick. The concentration, and thus the stability, of the anhydride solution has been monitored over a period of two weeks, and although the experiment is still in progress, the available data are compiled in Table VII.

TABLE VII

Stability of 0.078 M Triphenylacetic Oxalic Anhydride in Benzene at Room Temperature

<u>Age of Sample in Hours</u>	<u>A^a</u>	
	<u>l. mole⁻¹ cm.⁻¹</u>	<u>Anhydride (% of initial conc.)</u>
5	500.6	100
70.5	483.5	96.6
94	488.4	97.6
118	482.3	96.3
142	494.5	98.8
166	488.4	97.6
238	500.6	100
334	470.1	93.9

(a) molecular absorptivity at 1770 cm.⁻¹.

Light Measurements in Chemiluminescence

The procedure used to obtain the quantitative intensity, lifetime and quantum yield data summarized in Tables I and VI have been previously described⁸.

Attempted Modification of the Preparation of Triphenylacetic Oxalic Anhydride

Triphenylacetic acid (5.3 g., 0.02 moles) and triethylene-diamine (2.2 g., 0.02 moles) were combined with 250 ml. of benzene, and then last traces of water were removed by azeotropic distillation of 150 ml. of solvent. The remaining slurry was cooled to 25° under argon, and 1.9 g. (0.015 moles, 50% excess) of oxalyl chloride was added slowly with stirring. The reaction mixture was stirred 2 minutes, then filtered to remove insoluble material. The filtrate was evaporated to dryness under vacuum to obtain 3.6 g. (64%) of pale tan solid, which was identified by infrared spectroscopy as triphenylacetic anhydride. The product was found to be non-chemiluminescent when reacted with hydrogen peroxide in 1,2-dimethoxyethane in presence of DPA.

The above reaction was repeated at a reaction temperature of 5° to obtain 3.3 g. (60%) of triphenylacetic anhydride. The product was found to be non-chemiluminescent when reacted with hydrogen peroxide in 1,2-dimethoxyethane in presence of DPA.

Attempted Modification of the Preparation of Benzoic Oxalic Anhydride

Tetrabutylammonium oxalate (17.2 g., 0.03 moles), prepared by reaction of tetrabutylammonium hydroxide with oxalic acid, was slurried with 200 ml. of benzene; the last traces of water were removed by azeotropic distillation of 100 ml. of solvent. The remaining slurry was cooled to 25° under argon, and 8.4 g. (0.06 moles) of benzoyl chloride was added slowly with stirring. The reaction mixture was stirred one hour at 25° under argon, and then evaporated to dryness under vacuum to obtain a semi-solid yellow-brown material which was identified by infrared spectroscopy as a mixture of benzoic acid and benzoic anhydride (1:2), together with tetrabutylammonium chloride. Chemiluminescence tests on the material were negative.

4-Methoxybenzoic Oxalic Anhydride was prepared by the procedure reported for the preparation of bistriphenylacetic oxalic anhydride⁷. The reaction product was crystallized from anhydrous ether to obtain 0.7 g. (7.8%) of white crystals, m.p. 112-113°.

Anal. Calcd. for $C_{18}H_{14}O_8$: C, 60.34; H, 3.94. Found: C, 61.60; H, 4.16.

The 4-Methoxybenzoic oxalic anhydride was tested quantitatively for chemiluminescence and the results are given in Table II.

Preparation of Oxalate Esters

Most of the esters listed in Table III were prepared and purified by the procedure reported earlier for the preparation of phenyl oxalate⁷.

Compounds prepared by modified procedure:

Diphenylacetyl oxalate. - To a stirred solution of 15.5 gms. (0.1 mol of 2-chloroacetophenone and 4.5 gms. (0.05 moles) of anhydrous oxalic acid in 300 ml. of dry benzene was added 10.1 gms. (0.1 mole) of triethylamine. After stirring the mixture for four hours, the solid triethylamine-hydrochloride was filtered off and washed with benzene. The combined benzene liquors were then evaporated to dryness, yielding a solid which was washed with water and recrystallized from ethyl acetate. A crop of 2-chloroacetophenone (5 gms.) starting material was also recovered. See Table III for yield and product identification.

Diphenylmethyl phenyl oxalate. - Equivalent amounts of phenyl oxalyl chloride (3.7 gms., 0.02 moles) benzhydrol (3.68 gms., 0.02 mole) and triethylamine (2.02 gms., 0.02 mole) in 150 ml. of anhydrous ether were stirred for one hour. The triethylamine-hydrochloride was filtered off and the supernatant liquid evaporated. The oily product obtained crystallized on standing and was recrystallized from ether-petroleum ether mixture. See Table III for yield and product identification.

Phenyl oxalyl chloride was prepared according to the procedure of Stolle and Kuebel²³.

Bis(2,4-dinitrophenyl)oxalate. - Although this ester was prepared by the procedure reported earlier⁷, the work up of the crude product was modified due to the ready hydrolysis of the product. Minimal amount of water, about 100 ml. for 30 gms. of solid, was used to remove the triethylamine-hydrochloride. Dry ethyl acetate was used to free the product from any 2,4-dinitrophenol present. See Table III for yield and product identification.

Effect of Solvents on Chemiluminescence

Tests for chemiluminescence of bis(2,4-dinitrophenyl) oxalate were made on the following solvents, chosen because they were good solvents for the oxalate.

- a) acetone: S, but short half life.
- b) ethyl acetate: comparable to 1,2-dimethoxyethane.
- c) tetrahydrofuran + H₂O: M - MS.

Negative chemiluminescence with the following solvents:

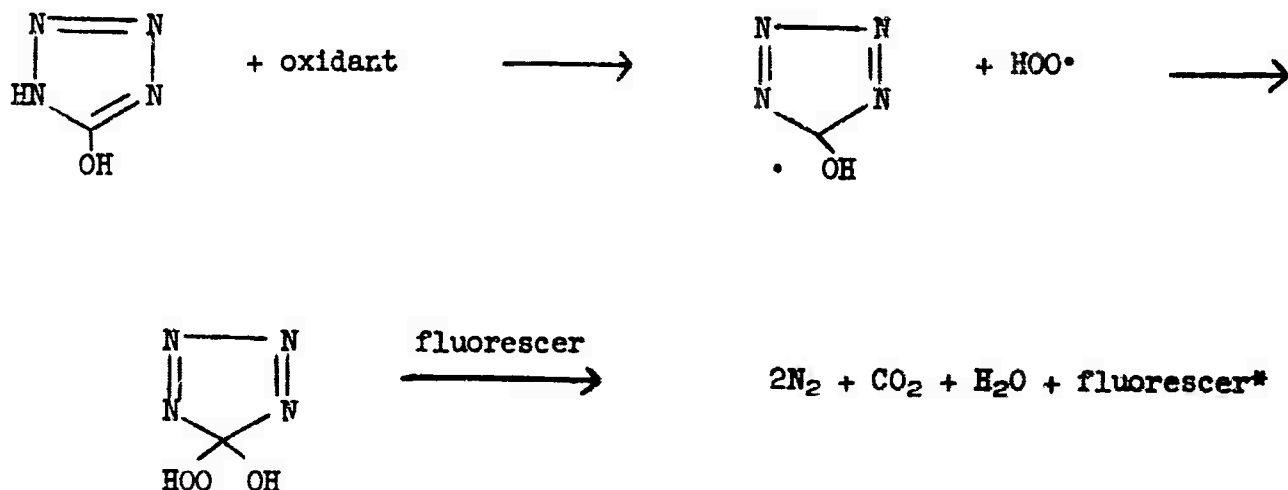
- a) dimethylsulfoxide
- b) hexamethylphosphoramide
- c) tetramethylurea.

Oxalyl dihydrazide-hydrogen peroxide-N-bromosuccinimide-DPA
system was tested by the addition of approximately 0.2 ml. anhydrous hydrogen peroxide in 1 ml. 1,2-dimethoxyethane to a 5 ml. solution of 3-5 mg. oxalyl dihydrazide and 3-5 mg. NBS and 1 mg. 9,10-diphenylanthracene in 1,2-dimethoxyethane. A brief medium intensity chemiluminescence was observed. Similar results were obtained when the NBS was replaced by t-butylhypochlorite.

SECTION III

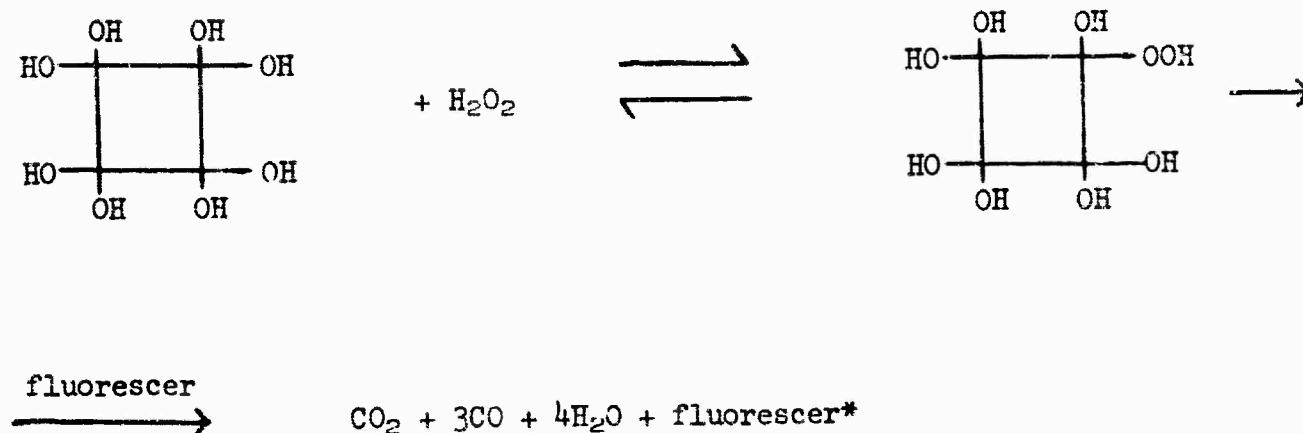
Exploratory Tests for Chemiluminescent Reactions

The possibility was examined that 5-hydroxytetrazole⁵⁵ might undergo chemiluminescent oxidation in the presence of a fluorescer according to the following reaction scheme.

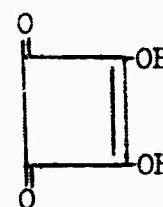
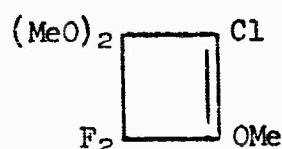
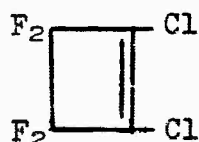


Chemiluminescence, however, was not observed under a variety of preliminary test conditions. Since the stability of the tetrazole ring is substantial⁵⁶, it seems likely that oxidation did not occur under the reaction conditions examined. Indeed, neither gas evolution nor other indications of reaction was observed in the experiments. Additional experiments will be carried out under more vigorous conditions.

The possibility was examined that octahydroxycyclobutane⁵⁷ might undergo chemiluminescent oxidation in the presence of a fluorescer according to the following reaction scheme.



Although substantial gas evolution was observed under the test conditions employed, light emissic was not seen. The intermediates listed below which were required for the synthesis of octahydroxycyclobutane were also examined for chemiluminescence under oxidizing conditions and under the test conditions used chemiluminescence was not seen.



Related experiments are planned.

SECTION III

EXPERIMENTAL

Materials

5-Hydroxytetrazole, m.p. 258-259°dec., lit.⁵⁵ 257-258°dec. was prepared by the method described by Lieber and Enkoj⁵⁵.

Diketocyclobutenediol and its precursor 1-chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene were prepared by the method of West, Miu and Ito⁵⁷.

Tetrahydroxy-1,4-quinone dihydrate was obtained from Aldrich Chemical Corporation.

Octahydroxycyclobutane

A solution of 2.0 g. (0.0175 mole) of diketocyclobutenediol in 50 ml. of water at 0° was treated dropwise with bromine until a faint yellow color persisted. The addition of 250 ml. of acetone precipitated the white crystalline product which was collected to yield 2.3 g. (73%), m.p. 139°dec., lit.⁵⁷ 140°dec.

Chemiluminescence Tests

The chemiluminescence experiments were done in 5 ml. of solvent with 2 mg. of the fluorescent acceptor, 5 mgs. of the compound to be tested, 0.2 ml. of 90% hydrogen peroxide and 0.05 ml. of trifluoroacetic acid or 5 mg. of potassium t-but

5-Hydroxytetrazole

A. Chemiluminescence tests of 5-hydroxytetrazole (ca. 10^{-3} M) were run in 0.5 M aqueous sodium hydroxide in the presence of sodium fluorescein. Chemiluminescence was not observed in experiments with 1) hemin and hydrogen peroxide, 2) potassium ferricyanide and hydrogen peroxide, 3) sodium hypochlorite and hydrogen peroxide and 4) with potassium persulfate. The hemin-hydrogen peroxide system was also examined in 0.1 N sodium carbonate with similar results.

B. A solution of ca. 10^{-3} M 5-hydroxytetrazole in dimethylsulfoxide with a trace of eosin was treated with potassium t-butoxide. Chemiluminescence was not observed. The addition of 5-hydroxytetrazole to a solution of sodium fluorescein in dimethylsulfoxide caused a complete bleaching of the color.

A negative test was also obtained in 1,2-dimethoxyethane with diphenylanthracene, potassium t-butoxide and 90% hydrogen peroxide.

Dichlorotetrafluorocyclobutene

Dichlorotetrafluorocyclobutene was tested for chemiluminescence in diethyleneglycol dimethyl ether with potassium t-butoxide and 90% hydrogen peroxide in the presence of 9,10-diphenylanthracene. There was no light detected. Trifluoroacetic acid and hydrogen peroxide in diethyleneglycol dimethyl ether with DPA produced a small amount of gas evolution with no detectable light.

1-Chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene

1-Chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene was reacted with hydrogen peroxide in a solution of DPA in glyme with potassium t-butoxide and with trifluoroacetic acid. Neither reaction produced light.

1-Chloro-3,3-difluoro-2,2,4,4-tetramethoxycyclobutane was tested under similar conditions with the same results.

Diketocyclobutenediol

Reactions of hydrogen peroxide and diketocyclobutenediol in water or 1,2-dimethoxyethane under acidic conditions (trifluoroacetic acid) or basic conditions (potassium t-butoxide) and with eosin or fluorescein did not produce detectable light. Under alkaline conditions in water, extensive gas evolution was observed. An experiment in dimethylsulfoxide with potassium t-butoxide and fluorescein was also negative.

Octahydroxycyclobutane

Octahydroxycyclobutane was tested with hydrogen peroxide in the presence of eosin, N-methyl-9-carbomethoxyacridinium bisulfate⁷ or quinine sulfate and trifluoroacetic acid. No light was seen.

The compound was also tested under basic conditions in the presence of fluorescein using hydrogen peroxide and 1) potassium hydroxide, 2) potassium t-butoxide or 3) hemin. All reactions produced extensive gas evolution with no detectable light. Sodium perborate was used in this system with similar results.

Octahydroxycyclobutane was tested under acidic and basic conditions in diethylene glycol dimethyl ether with diphenylanthracene. The reaction of hydrogen peroxide and *t*-butyl hydroperoxide with octahydroxycyclobutane in the presence of trifluoroacetic acid produced gas evolution but no detectable light. Experiments in diethylene glycol dimethyl ether with potassium hydroxide or potassium *t*-butoxide and hydrogen peroxide produced no observable light.

Octahydroxycyclobutane (ca. 5 mg.) was added to a solution of 1 M hydrogen peroxide in diethylene glycol dimethyl ether in the presence of DPA. There was extensive gas evolution observed but no light. This experiment was repeated at -70°C with similar results.

Octahydroxycyclobutane (ca. 5 mg) was added to a solution of dimethylphthalate and DPA at 140°. There was immediate and extensive gas evolution with no detectable light.

Tetrahydroxy-1,4-quinone dihydrate

The reaction of tetrahydroxy-1,4-quinone in diethylene glycol dimethyl ether with hydrogen peroxide in the presence of DPA and trifluoroacetic acid or potassium tertiary butoxide produced no detectable light.

UV Analysis of 9-Carboxy-10-methylacridinium Chloride and Its Pseudo Base

The ultraviolet spectrum of 9-carboxy-10-methylacridinium chloride in water and the spectrum of its pseudo base (sodium 10-methyl-9-hydroxyacridan-9-carboxylate) in 0.10 N aqueous sodium hydroxide are summarized below. The results reflect the expected loss of aromatic conjugation across the three ring system, resulting from pseudo base formation.

9-Carboxy-10-methylacridinium Chloride (2.0 x 10⁻⁵ molar in water)

Pseudo Base (2.0 x 10⁻⁵ molar in 0.10 N NaOH)

λ max.	Log ϵ	λ max.	Log ϵ
214	4.20	214	4.99
259	4.96	252	3.90
341	4.00	285	4.28
358	4.29	330(s)	3.78
399	3.63		
419	3.66		

Correction

Pages 25-26 are reversed in Chemiluminescent Materials, Technical Report No. 8.

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31. If induced decomposition were specified for step (6) the expected relation
ship would be of the form

$$1/Q = \frac{1}{K^1} \left[\left(1 + \frac{k_{10}}{k_9[R\cdot]} \right) + \left(\frac{k_6 k_{10}}{k_4 k_9} + \frac{k_6[R\cdot]}{k_4} \right) \frac{1}{[H_2O_2]} \right]$$

Thus one would expect a linear plot of $1/Q$ vs. $1/[H_2O_2]$ with the slope
increasing as $[R\cdot]$ increases.
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